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CORRELATIONAL ASPECTS OF SUBSTITUENT EFFECTS IN TRANSITION METAL COMPLEXES CONTAINING NON-FUSED PHENYL RINGS

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CONTENTS

ABBREVIATIONS

acac	acetylacetonate
btfac	benzoyltrifluoroacetonate
BE	binding energy
bipy	2,2′-bipyridine
H_2bae	bis(acetylacetone)ethylenediamine
$HBpz_3$	trispyrazoylborate
CT	charge transfer

DMF	N,N-dimethylformamide
DH	dimethylglyoximate
dtc	dithiocarbamate
diphos	1,2-diphosphinophenylethane
DMSO	dimethylsulfoxide
en	ethylenediamine
IP	ionization potential
py	pyridine
N-MeIm	N-methylimidazole
$P_2A{-}C_6H_4X$	pyrrole-2-carboxaldiminate
prol	prolinate
TCNE	tetracyanoethylene
THF	tetrahydrofuran
TPP	tetraphenylporphyrin
XTPP	tetrasubstituted tetraphenylporphyrin
tu	thiourea

A. INTRODUCTION

Correlational aspects of the Hammett equation [1] together with its ramifications have been reviewed [2—4] and are still the subject of discussion [5—7] as they relate to organic chemical systems. Substituent effects pertaining to metallocene derivatives having one or more substituted cyclopentadienyl rings have been briefly discussed as part of a more general review of electronic effects in such systems [8]. A recent non-exhaustive survey of linear free energy relationships in inorganic chemistry has also appeared [9] and to some extent is synergistic with the material surveyed herein.

The purpose of the present review is to focus attention on the various correlations that have been reported for transition metal complexes containing one or more substituted phenyl rings in order to provide an overall view of the manner in which the Hammett equation and its ramifications have been applied to such chemical systems. The use of various substituent constants in studies of complexes of the type, $(L^{Ar})_mML_n$ will be emphasized where L^{Ar} = a ligand bonded to the metal center, M. The phenyl ring in L^{Ar} may be bonded directly to the metal center via a metal—carbon bond in a monohapto, I, or hexahapto, II, manner or the phenyl ring in L^{Ar} may be separated from the metal center by one or more donor atoms or by part of the skeletal framework of the ligand, III. Q represents the donor atom(s) or the donor atom(s) plus the ligand skeletal framework and X represents one or more substituents on the phenyl ring.

Examples of the following types of correlation are included:

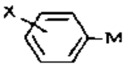
(i) the effect of X on a property or the reactivity of the co-ligands, L.

(ii) the effect of X on a property or the reactivity of L^{Ar}.

(iii) the effect of X on a property or a reactivity pattern associated with the entire complex.

(iv) the effect of X on a property associated primarily with the metal center, M.

(v) substituent effects associated with the reactivity of a ligand, L^{Ar}, towards a given metal center.



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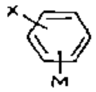

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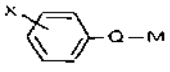


III

Within the foregoing terms of reference this review is reasonably comprehensive and surveys the pertinent and most accessible literature through June 1979.

B. COMPLEXES CONTAINING A SUBSTITUTED PHENYL RING DIRECTLY BONDED TO A METAL CENTER

(i) Complexes containing a hexahapto bonded phenyl ring

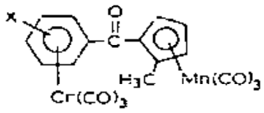
Substituent effects associated with hexahapto bonded phenyl rings have been most extensively studied via physicochemical methods utilizing complexes of the type, (arene) $Cr(CO)_3$ where arene is a mono- or polysubstituted benzene ring.

The existence of a qualitative relationship between the ν(CO) frequencies for (arene) $Cr(CO)_3$ complexes and the Hammett σ parameters was first noted by Fischer [10]. Several related studies have since been reported [11—19]. The Cotton-Kraihanzel force constants, k_{CO} [20] for a number of (substituted methylbenzoate) $Cr(CO)_3$ derivatives have been linearly correlated to the Hammett σ_p parameter as $\Sigma\sigma_p$ [10]. The Hammett σ_p parameter was regarded to best represent both the inductive and mesomeric effects of the substituents. However, no direct correlation was observed between this parameter and the ester carbonyl frequencies. The quantity k_{CO} has also been linearly correlated to the first ionization potential of a number of (arene) $Cr(CO)_3$ derivatives [12]. The ionization potential decreased as the arene became more electron-releasing. More recently, k_{CO} has been shown to be a linear function of Taft's σ_I parameter for a series of (substituted benzene) $Cr(CO)_3$ complexes [13]. In fact, two linear relationships were noted. The first of these involves only those substituents having a lone pair of electrons and the second takes into account only those substituents bonded to the benzene ring via a carbon atom. This is not an unexpected result since the first ionization potentials for the same series of complexes can also be expressed as two linear functions of σ_I according to

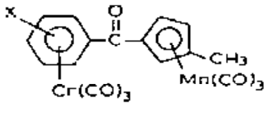
$$E_{Cr-R} = 7.19 + 1.15\ \Sigma\sigma_I(R) \tag{1}$$

$$E_{Cr-X} = 6.94 + \Sigma\sigma_I(X) \tag{2}$$

where R represents a substituent bonded to the phenyl ring via a carbon atom, X represents a substituent having a lone pair of electrons and E_{Cr-R}, E_{Cr-X} are the corresponding ionization potentials (eV) respectively. The energy required to disassociate a CO group from (arene) $Cr(CO)^+$ and (arene) $Cr(CO)_2^+$ species decreases with increasing value of k_{CO} (and σ_p) but increases with increasing value of k_{CO} (and σ_p) for (arene) $Cr(CO)_3^+$ species [14]. No clear explanation for this observation is presently available. The ν(CO) frequency (E mode) for a number of (substituted fluorobenzene) $Cr(CO)_3$ derivatives may be correlated to both σ_p or to a combination of Swain-Lupton [21] field and resonance parameters [15]. Wu et al. have observed that ν(CO) shows a better correlation with σ_p than σ_m in a series of (*m*- and *p*-substituted aniline) $Cr(CO)_3$ complexes [16]. Neuse [17] has reported the results of a statistical study of the degrees of correlation attainable between k_{CO} and selected Hammett and Taft parameters, σ_I, σ_p, $\sigma_p - \sigma_I$, $\sigma_p^0\sigma_R^0$ and has concluded that for a large number of mono- and polysubstituted benzene derivatives of $Cr(CO)_3$ that the overall electronic substituent effect transmitted to the carbonyl ligands involves both an inductive and resonance mechanism. The quantity, $\Delta K(CO) = k_{CO}(H) - k_{CO}(X)$ has also been correlated to Hammett's σ parameter for a large number of (alkylsubstituted benzene) $Cr(CO)_3$ complexes [18] where $k_{CO}(H)$ and $k_{CO}(X)$ are the force constants for the unsubstituted and substituted derivatives respectively. The $\Delta\nu$(CO) and ΔK(CO) values for about forty derivatives of the type, (substituted methyl benzoate) $Cr(CO)_3$ [19] have also been correlated in terms of a Yukawa-Tsuno equation [7,22]. As noted previously [11] a poor correlation was also observed with the ester carbonyl frequencies for this extended series of complexes. Conformational effects are considered to be responsible for this lack of any direct correlation [23]. The ν(CO) frequencies of the $Cr(CO)_3$ moiety for the derivatives, IV and V where X = H, 2-CH_3, 3-CH_3, 4-CH_3 or 4-OCH_3 have been reported to be sensitive to the nature of X, whereas the ν(CO) frequencies of the $Mn(CO)_3$ moiety are not affected [24]. The changes in ν(CO) follow the expected pattern.



IV



V

Various NMR techniques have been used to probe substituent effects in (arene) $Cr(CO)_3$ complexes [15,25—30]. Mangini and Taddei [25] have correlated free arene ^1H NMR chemical shifts with the corresponding chemical shifts in a series of $(\eta^6\text{-}XC_6H_5)Cr(CO)_3$ and $(\eta^6\text{-}XC_6H_4CH_3)Cr(CO)_3$ complexes where X = $N(CH_3)_2$, OCH_3, SCH_3, H, CH_3, CO_2CH_3, and $COCH_3$. An approximately linear variation of the change on complex formation of the *meta*-substituent parameter, $\Delta S(m{-}X) = S^c(m{-}X) - S^f(m{-}X)$, with Taft's resonance parameter, σ_R for various substituents X has been noted for a series of (substituted toluene)$Cr(CO)_3$ derivatives [26]. The significance of this particular correlation is open to question since the method of calculating $\Delta S(m\text{—X})$ has been criticized [27]. Fritz and Kreiter [28] have reported the results of a detailed ^{1}H NMR study (ring protons and methyl protons) for the complexes $(\eta^6\text{-XC}_6\text{H}_4\text{Y})\text{M(CO)}_3$ where M = Cr, Mo or W, and X, Y = various 1,4-substitutions of F, Cl, Br, OH, NH_2, OCH_3, SCH_3, $N(CH_3)_2$, $Si(CH_3)_3$, $COCH_3$ or CH_3 groups on the benzene ring and concluded that the $M(CO)_3$ moiety exerted a levelling effect on the distribution of electron density in the coordinated arene ligand. The amine proton chemical shifts for a series of (*m*- and *p*-substituted aniline)$Cr(CO)_3$ derivatives yielded straight lines when plotted versus the Hammett σ and σ^- parameters for the substituents [16]. Such plots were interpreted as being consistent with the presence of a direct resonance interaction between the substituents and the amino nitrogen atom as observed for the corresponding uncomplexed anilines [31,32]. The slopes of these plots were greater for the free anilines than the complexed anilines indicating that in the complexes the electron density at nitrogen was less sensitive to the nature of the substituent because of the electron-withdrawing effect of the $Cr(CO)_3$ group.

The ^{19}F NMR chemical shifts for (substituted fluorobenzene)$Cr(CO)_3$ derivatives have been correlated to a combination of Swain-Lupton field and resonance parameters [15].

Plots of $\delta(\text{C}para)$ versus σ^+ for $(\eta^6\text{-XC}_6\text{H}_5)\text{Cr(CO)}_3$ derivatives (X = H, CH_3, C_2H_5, OCH_3, $C(CH_3)_3$ or $COCH_3$) obtained at 25°C and −76°C have been used to study the conformational equilibria present in solution [29]. It was concluded from these data that complexation did not significantly change the transmission of electronic effects to the *para* position. A detailed analysis of the same ^{13}C NMR shifts for the series of $(\eta^6\text{-XC}_6\text{H}_5)\text{Cr(CO)}_3$ complexes (X = H, F, Cl, CH_3, OCH_3, OC_4H_9, CO_2CH_3, NH_2, $N(CH_3)_2$) also revealed that there was no significant change in the transmission of resonance effects in going from the free arene to the complexed arene [27].

For the complexes, $(\text{C}_6\text{H}_{6-n}\text{Y}_n)\text{Cr(CO)}_2\text{(CX)}$ where X = O or S; Y = H, Cl, CH_3, OCH_3, NH_2, $N(CH_3)_2$ or $COCH_3$; n = 0—3, a linear regression analysis shows a good linear correlation between $\delta(^{13}\text{CO})$ and k_{CO} but not with $\delta(^{13}\text{CS})$ or $\delta(\text{C}^{17}\text{O})$ [30]. The precise reason for this different behaviour is not readily apparent.

The $\pm 3/2 \rightleftharpoons 5/2$ NQR transition of ^{55}Mn has been observed to correlate with the number of methyl groups in the complexes, $[(\eta^6\text{-(CH}_3)_n\text{C}_6\text{H}_{6-n})\text{Mn(CO)}_3]^+$ [33] and that this behaviour paralleled the changes in ν(CO) for $(\eta^6\text{-(CH}_3)_n\text{C}_6\text{H}_{6-n})\text{Cr(CO)}_3$ complexes with respect to the number of methyl groups [10].

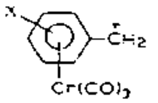
The linear correlation given by

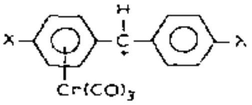
$$\epsilon = 1400\ \Sigma\ \sigma_p^+ + 10100 \qquad (3)$$

between the extinction coefficient of the lowest energy absorption band for a large number of (substituted arene)$Cr(CO)_3$ derivatives has been reported [34]. This particular correlation has been interpreted in terms of the origin of the electronic transition involving a charge transfer from the central chromium atom to the arene ligand. For a number of complexes of the type, $(\eta^6\text{-}XC_6H_5)\text{-}Cr(CO)_3 \cdot TCNE$ (TCNE = tetracyanoethylene), the observed charge transfer frequencies have been linearly correlated to the σ^+ parameter of X, a result which is consistent with the presence of a charge transfer interaction between TCNE and the coordinated arene [35].

The pK_a values for a number of $(\eta^6\text{-}XC_6H_4OH)Cr(CO)_3$ complexes (X = 4-CH_3, H, 3-O_2CCH_3, 3-$COCH_3$, 4-O_2CCH_3 or 4-OCH_3) have been determined in 50% ethanol and have been shown to be linear functions of σ(σ^- for X = $COCH_3$ and O_2CCH_3) with a slope = 0.99 [36]. The corresponding slope for the uncoordinated phenol was 2.51 indicating that the free phenol is more sensitive to substituent effects than the complexed phenol. This result is similar to that observed for analogous complexes containing a substituted aniline in place of the phenol [16]. The thermodynamic dissociation constants for several (substituted benzoic acid) $Cr(CO)_3$ complexes have been determined in 50% ethanol and the pK_a values correlated in terms of the Yukawa-Tsuno equation [37]. The reaction constant for the free benzoic acids was found to be 1.4 which decreased to 0.8 for the corresponding complexed acid. This is a further reflection of the decreased ability of the complexed ring to transmit the electronic effects of the substituent as a consequence of the presence of the $Cr(CO)_3$ group.

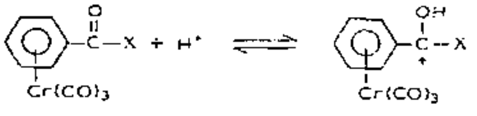
The pK_{R^+} values for complexed benzyl carbonium ions, VI, (X = H, Cl,


VI


VII

CH_3 or OCH_3) correlate well with σ^- (ρ = —5.1) but not with the σ^+ parameter which suggests that there is a different interaction between the complexed aromatic ring and the positive carbon center as compared to the uncomplexed carbonium ion [38].

Somewhat similar results have recently been reported for VII [39] where the pK_{R^+} values exhibited poor correlations with both the σ and σ^+ parameters in going from the free carbonium ion to the complexed carbonium ion. For the protonation reaction


(4)

where X = $N(CH_3)_2$, OH, CH_3, C_6H_5 or H, the quantity ΔpK_{BH^+} was found to be reasonably linear with respect to σ_p^+(ρ = —1.72) or σ_p(ρ = —3.39) but not linear with respect to σ_m [40]. The quantity ΔpK_{BH^+} = pK_{BH^+} (free) — pK_{BH^+} (complexed) and pK_{BH^+} = —log K for the reverse of reaction (4). These particular correlations are consistent with the notion that the $Cr(CO)_3$ group is electron-withdrawing and is capable of assisting the aromatic ring in the stabilization of the benzyl cation.

The effect of substituents on the rate of ligand exchange in (η^6-XC_6H_5)M-$(CO)_3$ complexes where M = Cr, Mo or W and X = H, Cl, CH_3 has been reported [41]. The rate of exchange for reaction (5) is given by eqn. (6).

$$(\eta^6\text{-}XC_6H_5)M(CO)_3 + {}^{14}C_6H_5X \rightarrow (\eta^6\text{-}{}^{14}C_6H_5X)M(CO)_3 + XC_6H_5 \qquad (5)$$

$$\text{Rate} = k_2[(\eta^6\text{-}XC_6H_5)M(CO)_3]^2 + k_2'[(\eta^6\text{-}C_6H_5X)M(CO)_3][{}^{14}C_6H_5X] \qquad (6)$$

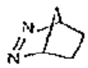
The mechanism of exchange was discussed taking into account that log k_2 and log k_2' are each linear functions of Hammett's σ_p parameter. A Hammett correlation between log(k/k_0) and σ has been briefly reported for the ion molecule reaction (7) [42]

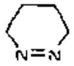
$$(\text{arene})Cr(CO)_3^+ + (\text{arene})Cr(CO)_3 \rightarrow (\text{arene})_2Cr_2(CO)_3^+ + 3\ CO \qquad (7)$$

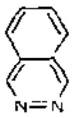
The alkaline hydrolysis in aqueous acetone for (substituted methylbenzoate)-$Cr(CO)_3$ complexes proceeds at a much greater rate than the corresponding hydrolysis of the uncomplexed ester [43]. Good correlations were observed when log k was plotted versus σ. The reaction constant for the complexed ester was found to be 1.55 as compared to 2.36 for the corresponding free ester. The reduced reaction constant for the complexes may again be attributed to the electron-withdrawing $Cr(CO)_3$ group. The rates of reaction in acetone between NaSCN and $XC_6H_4CH_2Cl$ as well as (η^6-$XC_6H_4CH_2Cl$)Cr-$(CO)_3$ have been compared [44]. Non-linear Hammett plots of log k versus σ were obtained in each case and were discussed in terms of the electron-withdrawing and electron-releasing ability of the $Cr(CO)_3$ moiety. The rate of acetolysis at 75°C of a series of 2-aryl-2-methyl-1-propyl-methanesulfonates complexed to $Cr(CO)_3$ have been correlated to Hammett's σ^+ parameter with a reaction constant, $\rho = -0.78$ which is much smaller than $\rho = -2.35$ which was observed for the corresponding uncomplexed methanesulfonate [45]. This difference in reactivity has been discussed in terms of the buffering action of the $Cr(CO)_3$ group. The pattern of substituent effects in the complexes, (η^6-$XC_6H_4C{\equiv}CMR_3$)$Cr(CO)_3$ where X is one of 2-, 3- or 4-CH_3, OCH_3, Cl, H or CF_3; M = Si, R = CH_3 or M = Ge, R = C_2H_5 was studied by measuring the rate of cleavage of the C—M bond in aqueous potassium hydroxide [46]. Plots of log k_X/k_H versus σ parameters were discussed and support the conclusion that the $Cr(CO)_3$ moiety causes little distortion in the normal pattern of substituent effects observed for an uncomplexed arene. The second order rate constants, k_2, for the displacement of the coordinated arene by $P(OCH_3)_3$ in the complexes, (arene)$W(CO)_3$ (arene = $CH_3CO_2C_6H_5$, C_6H_6, $CH_3C_6H_5$ or 1,3,6-$(CH_3)_3C_6H_3$) have been correlated to the $\nu(CO)(A_1)$ mode in the IR [47] but no firm interpretation could be associated with this correlation since the rates of reaction when the arene was $(CH_3)_2NC_6H_5$ and $CH_3OC_6H_5$ were higher than expected.

The transmission of electronic effects to the CO groups in a number of complexes of the type (arene)$Cr(CO)_2L$ (L = maleic anhydride (ma), 2,3-diazobicyclo[2.2.1]hept-2-ene (az), phthalazine (phz) and pyridazine (pdz)) have been studied by Herberhold and his co-workers [48—50]. Plots of k_{CO} versus

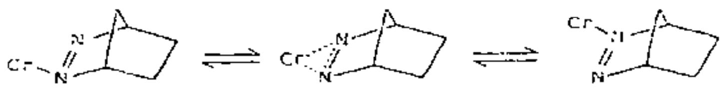

ma


az


pdz


phz

$\Sigma\sigma_p$ for the substituents of the aromatic ring were discussed. For the maleic anhydride derivatives, no correlation was observed with σ_m or the Taft constants, σ_R and σ_I nor was there any correlation between the NMR spectral parameters of the olefin and k_{CO} or $\Sigma\sigma_p$. However, there was a good linear relationship between the higher ν(C=O) frequency of the anhydride ligand and k_{CO} as well as $\Sigma\sigma_p$ [48]. The azo ligands were unsymmetrically bonded to chromium and for L = az, the azo ligand was shown to be mobile on the NMR time scale as shown in eqn. (8).



(8)

A linear plot of $\Delta G^{\ddagger}$ versus $\Sigma\sigma_p$ was also noted for this process, $\Delta G^{\ddagger}$ increasing as the arene becomes electron-rich as a consequence of the effect of the substituent [49].

The proton NMR spectra in acetone have been recorded for a series of arene (cyclopentadienyl) iron complexes, $[(\eta^6\text{-}XC_6H_5)(\eta^5\text{-}C_5H_5)Fe]^+$ and $[(\eta^6\text{-}4\text{-}XC_6H_4CH_3)(\eta^5\text{-}C_5H_5)Fe]^+$ (X = NH_2, CH_3, C_2H_5, OCH_3, $NHCOCH_3$, Cl, F, CN, H, CO_2H, $CO_2C_2H_5$, $CONH_2$ or OC_6H_5) and the chemical shifts subjected to a detailed correlational analysis using sets of Hammett-Taft σ parameters [51]. The major conclusion from this analysis was that the substituents on the arene ring exhibit similar effects whether the ring is free or coordinated to the metal center.

The polarographic reduction potential, $E_{1/2}$ for the process shown in eqn. (9) has been determined in acetonitrile and has been related to the Taft polar constant, $\sigma_p{}^0$, by eqn. (10) [52].

$$[(\eta^6\text{-}4\text{-}XC_6H_4CH_3)(\eta^5\text{-}C_5H_5)Fe]^+ + e^- \rightleftharpoons [(\eta^6\text{-}4\text{-}XC_6H_4CH_3)(\eta^5\text{-}C_5H_5)Fe] \qquad (9)$$

$$E_{1/2} = -1.42 + 0.515\,\sigma_p{}^0 \qquad (10)$$

The potential becomes more negative as X becomes more electron releasing.

Electrochemical studies have also been reported for bis(arene)chromium(0) complexes [53,54]. Klabunde has reported that $E_{1/2}$ for the electrochemical oxidation in acetonitrile of a series of complexes, $(arene)_2Cr$ where arene is $C_6H_5OCH_3$, C_6H_5F, C_6H_6, $C_6H_5CF_3$, 2,5-$(CH_3)_2C_6H_3Cl$, $C_6H_5CH_3$, $(C_6H_5)_2$, 1,4-$ClC_6H_3CF_3$, 2-$CF_3C_6H_4Cl$, or 1,4-$(CF_3)_2C_6H_4$ [53] is a linear function of σ_p. The good quality of this correlation implies a significant involvement of

TABLE 1

Summary of correlations involving hexahapto bonded substituted phenyl rings

Chemical system	Correlation	Ref.
$(\eta^6\text{-XC}_6\text{H}_4\text{CO}_2\text{CH}_3)\text{Cr(CO)}_3$ X = 3-CO_2CH_3, 4-CO_2CH_3, 3-Cl, 4-Cl, 2-Cl, H, 3-CH_3, 4-CH_3, 2-CH_3, 4-OCH_3, 2-OCH_3, 4-NH_2	k_{CO} (mdyne A^{-1})/$\Sigma\sigma_p$	11
X = H, 2-CH_3, 2-C_2H_5, 2-i-C_3H_7, 2-t-C_4H_9, 2-OCH_3, 3-CH_3, 3-C_2H_5, 3-i-C_3H_7, 3-t-C_4H_9, 3-OCH_3, 3-C_6H_5, 3-F, 3-Cl, 3-Br, 3-CO_2CH_3, 3-CF_3, 4-CH_3, 4-C_2H_5, 4-neo-C_5H_{11}, 4-i-C_3H_7, 4-t-C_4H_9, 4-$\text{C(C}_2\text{H}_5)_3$, 4-$\text{N(CH}_3)_2$, 4-$\text{OCH}_3$, 4-$\text{C}_6\text{H}_5$, 4-Cl, 4-$\text{CO}_2\text{CH}_3$, 4-$\text{CF}_3$, 2,4,6-$(\text{CH}_3)_3$, 3,4-$(\text{OCH}_3)_2$, 3,5-$(\text{CH}_3)_2$, 3,5-t-$\text{C}_4\text{H}_9$, 3,5-$(\text{OCH}_3)_2$, 3,5-$\text{Cl}_2$, 3,4,5-$(\text{OCH}_3)_3$, 3-($\pi$-[$\text{Cr(CO)}_3$]$\text{C}_6\text{H}_5$), 4-($\pi$[$\text{Cr(CO)}_3$]$\text{C}_6\text{H}_5$)	$\Delta\nu(\text{CO})\,(\text{cm}^{-1}) = \rho(\sigma^n + r\Delta\sigma_R^+) + a$ $K(\text{CO})$ (mdyne A^{-1}) = $\rho(\sigma_p^n + r\Delta\sigma_R^+) + K(\text{CO})_0$	19
$(\eta^6\text{-XC}_6\text{H}_4\text{CO}_2\text{CH}_3)\text{Cr(CO)}_3/\text{OH}^-$ X = 4-CO_2CH_3, 3-CO_2CH_3, 4-Cl, 3-Cl, H, 4-CH_3, 3-CH_3, 2-CH_3, 4-OCH_3, 4-NH_2	log k/σ ρ = +1.55 (56% aq. acetone)	43
$[(\eta^6\text{-XC}_6\text{H}_4\text{CO}_2\text{CH}_3)\text{Cr(CO)}_3] \xrightarrow{e^-} [(\eta^6\text{-XC}_6\text{H}_4\text{CO}_2\text{CH}_3)\text{Cr(CO)}_3]^-$ X = 4-NH_2, 4-OH, 4-OCH_3, 4-CH_3, 3-CH_3, 4-F, H, 4-C_6H_5, 3-OCH_3, 3-F, 4-CO_2CH_3	$E_{1/2}$ (V)/σ ρ = +0.49 V (DMF)	56
$(\eta^6\text{-XC}_6\text{H}_5)\text{Cr(CO)}_3$ X = OCH_3, 1,3-$(\text{OCH}_3)_2$, 1,4-$(\text{OCH}_3)_2$, 1,2-$(\text{OCH}_3)_2$, 1,2,3-$(\text{OCH}_3)_3$, 1,2,4-$(\text{OCH}_3)_3$, 1,3,5-$(\text{OCH}_3)_3$	k_{CO} (mydne A^{-1})/$\Sigma\sigma_p$	11
X = F, COCH_3, CO_2CH_3, Br, Cl, I, H, C_6H_5, CH_3, $\text{Si(CH}_3)_3$, OCH_3, $\text{C(CH}_3)_3$, NH_2, $\text{N(CH}_3)_2$, 1,3,5-$(\text{CH}_3)_3$, 1,4-$(\text{N(CH}_3)_2)_2$	I.E. (eV)/k_{CO} (mdyne A^{-1})	12
X = COCH_3, CO_2CH_3, C_6H_5, H, CH_3, $\text{C(CH}_3)_3$, 1,3,5-$(\text{CH}_3)_3$, 1,2,3,4,5,6-$(\text{CH}_3)_6$	I.E. (eV)/$\Sigma\sigma_I$	13
X = F, Cl, Br, I, CO_2CH_3, OCH_3, OH, NH_2, $\text{N(CH}_3)_2$	I.E. (eV)/$\Sigma\sigma_I$	13
X = H, CH_3, C_2H_5, OCH_3, $\text{C(CH}_3)_3$, COCH_3	$\delta(^{13}\text{C}\ para)(\text{ppm})/\sigma^*$	29
X = $\text{N(CH}_3)_2$, 1,2,3,4,5,6-$(\text{CH}_3)_6$, 1,2,4,5-$(\text{CH}_3)_4$, 1,3,5-$(\text{CH}_3)_3$, OCH_3, 1,4-$(\text{CH}_3)_2$, CH_3, F, H, $\text{Si(C}_2\text{H}_5)_3$, Cl, $\text{CO}_2\text{C}_2\text{H}_5$	$\epsilon = 1400\Sigma\sigma_p^+ + 10100$	34
X = H, C_2H_5, CH_3, neo-C_5H_{11}, i-C_3H_7, t-C_4H_9, $\text{C(C}_2\text{H}_5)_3$, $\text{CH(t-C}_4\text{H}_9)_2$, OCH_3, $\text{Si(CH}_3)_3$, C_6H_5, F, CO_2CH_3, CF_3, 1,2-$(\text{CH}_3)_2$, 1,2-$(\text{C}_2\text{H}_5)_2$, 1,2-(neo-$\text{C}_5\text{H}_{11})_2$, 1,2-(i-$\text{C}_3\text{H}_7)_2$, 1,2-(t-$\text{C}_4\text{H}_9)_2$, 1,2-$(\text{Si(CH}_3)_3)_2$, 1,3-$(\text{CH}_3)_2$, 1,3-(t-$\text{C}_4\text{H}_9)_2$, 1,3-$(\text{Si(CH}_3)_3)_2$, 1,4-(t-$\text{C}_4\text{H}_9)_2$, 1,4-$(\text{Si(CH}_3)_3)_2$, 1-$\text{CH}_3$-3,5-(t-$\text{C}_4\text{H}_9)_2$, 1,2,4-	$\Delta K(\text{CO})(\text{mdyne A}^{-1})^{a}/\sigma$	18

TABLE 1 (Continued)

Chemical system	Correlation	Ref.
$(\text{t-}C_4H_9)_3$, 1,3,5-$(C_2H_5)_3$, 1,3,5-$(\text{neo-}C_5H_{11})_3$, 1,3,5-$(\text{i-}C_3H_7)_3$, 1,3,5-$(\text{t-}C_4H_9)_3$ X = H, CH_3, C_2H_5, i-C_3H_5, C_6H_5, OCH_3, OC_2H_5, OC_5H_5, NH_2, $N(CH_3)_2$, C_6H_5CO, CO_2CH_3, Br, Cl, 1,4-$(OCH_3)_2$, 1,4-$(OC_2H_5)_2$, 1,4-$(NH_2)_2$, 1-F-4-CH_3, 1-NH_2-4-COC_6H_5, 2-NH_2-3-CH_3, 1-NH_2-4-CH_3, 1,2-$(OCH_3)_2$, 1,3,5-$(CH_3)_3$	k_{CO} (mdyne A^{-1})/$\sigma_I, \sigma_p, \sigma_p - \sigma_I, \sigma_p^0, \sigma_R^0$	17
$(\eta^6\text{-}XC_6H_4F)Cr(CO)_3$ X = H, 4-CH_3, 4-OCH_3, 4-Cl, 4-NH_2, 4-F, 4-CF_3, 3-CH_3, 3-OCH_3, 3-Cl, 3-NH_2, 3-F, 3-CF_3	$\nu(CO)$ (cm^{-1})/σ_p $\nu(CO)$ (cm^{-1})/35% $\mathcal{F}$ + 65%$\mathcal{F}$ $\delta(^{19}F)$ (ppm)/6%$\mathcal{R}$ + 94%$\mathcal{R}$	15
$(\eta^6\text{-}XC_6H_4NH_2)Cr(CO)_3$ X = H, 3-Cl, 4-Cl, 3-CH_3, 4-CH_3, 3-OCH_3, 4-OCH_3, 3-CO_2CH_3, 4-CO_2CH_3, 4-$COCH_3$	$\nu(CO)$ (cm^{-1})/σ_p $\delta(NH_2)$ (ppm)/σ, σ^-	16
$(\eta^6\text{-}XC_6H_5)Cr(CO)_3$, $(\eta^6\text{-}XC_6H_4CH_3)Cr(CO)_3$ X = $N(CH_3)_2$, OCH_3, SCH_3, H, $COCH_3$, CO_2CH_3, CH_3	τ(arene)/τ(complex)	25
$(\eta^6\text{-}4\text{-}XC_6H_4CH_3)Cr(CO)_3$ X = F, Cl, Br, OH, NH_2, OCH_3, SCH_3, $N(CH_3)_2$, $Si(CH_3)_3$, CO_2CH_3, $CH(OC_2H_5)_2$, CHO, CH_3	$\Delta S(m\text{-}X)^b/\sigma_R$	26
$(\eta^6\text{-}XC_6H_4OH)Cr(CO)_3$ X = 4-CH_3, H, 3-CO_2CH_3, 3-CH_3CO, 4-CO_2CH_3, 4-CH_3CO	$pK_a/\sigma, \sigma^-$ $\rho = 0.99$ (50% ethanol)	36
$(\eta^6\text{-}XC_6H_4CO_2H)Cr(CO)_3 \rightleftharpoons H^+ + (\eta^6\text{-}XC_6H_4CO_2)Cr(CO)_3^-$ X = 2-CH_3, 2-C_2H_5, 2-i-C_3H_7, 2-OCH_3, 3-CH_3, 3-C_2H_5, 3-i-C_3H_7, 3-t-C_4H_9, 3-OCH_3, 3-C_6H_5, 3-F, 3-Cl, 3-Br, 3-CO_2H, 3-CF_3, 4-CH_3, 4-C_2H_5, 4-neo-C_5H_{11}, 4-i-C_3H_7, 4-t-C_4H_9, 4-$C(C_2H_5)_3$, 4-$N(CH_3)_2$, 4-C_6H_5, 4-Cl, 4-CO_2H, 4-CF_3, 3-$(\pi[Cr(CO)_3]C_6H_5)$, 4-$(\pi\text{-}[Cr(CO)_3]C_6H_5)$, 2,4,6-$(CH_3)_3$, 3,4-$(OCH_3)_2$, 3,5-$(CH_3)_2$, 3,5-$(\text{t-}C_4H_9)_2$, 3,5-$(OCH_3)_2$, 3,4,5-$(OCH_3)_3$	$\log K/K_0 = \rho(\sigma + r\Delta\sigma_R^+)$ $\rho = 0.8$ (50% ethanol)	37
$(\eta^6\text{-}(CH_3)_nC_6H_{6-n})Cr(CO)_3$ $n = 0$—6	$\nu(CO)$ (cm^{-1})/n	33
$(\eta^6\text{-}(CH_3)_nC_6H_{6-n})Mn(CO)_3^+$ $n = 0, 1, 2, 3, 5$ or 6	$\pm 3/2 \rightleftharpoons 5/2$ $^{55}Mn/n$	33

TABLE 1 (continued)

Chemical system	Correlation	Ref.
TCNE · $(\eta^6\text{-XC}_6\text{H}_5)\text{Cr(CO)}_3$ X = NH_2, $(\text{CH}_3)_6$, $\text{N(CH}_3)_2$, 1,2,4,5-$(\text{CH}_3)_4$, 1,3,5-$(\text{CH}_3)_3$, OCH_3, 1,2-$(\text{CH}_3)_2$, 1,3-$(\text{CH}_3)_2$, 1,4-$(\text{CH}_3)_2$, C_2H_5, CH_3, Ge-$(\text{C}_2\text{H}_5)_3$, F, $\text{Si(C}_2\text{H}_5)_3$, H, Cl, Br, I, CO_2H, CO_2CH_3, $\text{CO}_2\text{C}_2\text{H}_5$	$\overline{\nu}_{\text{CT}}$ (cm^{-1})/σ^+	35
$(\eta^6\text{-XC}_6\text{H}_5)\text{Cr(CO)}_2\text{L}$ L = 2,3-diazabicyclo[2.2.1]hept-2-ene X = H, 1,2,3,4,5,6-$(\text{CH}_3)_6$, 1-CH_3-4-$\text{N(CH}_3)_2$, 1,3,5-$(\text{CH}_3)_3$, 1,4-$(\text{CH}_3)_2$, 1-CH_3-4-OCH_3, 1-CH_3-4-CO_2CH_3, 1,4-$(\text{CO}_2\text{CH}_3)_2$	k_{CO} (mdyne A^{-1})/$\Sigma\sigma_p$	49
	$\Delta G^\ddagger$ (kcal/mol^{-1})/$\Sigma\sigma_p$	49
$(\eta^6\text{-XC}_6\text{H}_5)\text{Cr(CO)}_i^+$ i = 1, 2 or 3 X = Cl, CO_2CH_3, CH_2OH, H, CH_3, OCH_3, 1,2-$(\text{CH}_3)_2$, 1,3,5-$(\text{CH}_3)_3$, NH_2, 1,2,3,4,5,6-$(\text{CH}_3)_6$	D_i^{c} (eV)/$\Sigma\sigma_p$, k_{CO}(mdyne A^{-1})	14
$(\eta^6\text{-4-XC}_6\text{H}_4\text{CH}_2\text{OH})\text{Cr(CO)}_3 + \text{H}^+ \rightleftharpoons$ $(\eta^6\text{-4-XC}_6\text{H}_4\text{CH}_2)\text{Cr(CO)}_3^+ + \text{H}_2\text{O}$ X = H, Cl, CH_3, OCH_3	$\text{p}K_{\text{R}}^+/\sigma$ ρ = 0.51 (aq. acetone)	38
$(\eta^6\text{-XCOHC}_6\text{H}_5)\text{Cr(CO)}_3^+ \rightleftharpoons \text{H}^+ +$ $(\eta^6\text{-XCOC}_6\text{H}_5)\text{Cr(CO)}_3$ X = H, C_6H_5, CH_3, OH, $\text{N(CH}_3)_2$	$\Delta\text{p}K_{\text{BH}^+}{}^{\text{d}}/\sigma_p$, σ_p $\rho = -1.72(\sigma_p^+)$	40
$(\text{arene})\text{Cr(CO)}_3^+ + (\text{arene})\text{Cr(CO)}_3 \rightarrow$ $(\text{arene})_2\text{Cr}_2(\text{CO})_3^+ + 3\ \text{CO}$ arene = $(\text{CH}_3)_6\text{C}_6$, $\text{NH}_2\text{C}_6\text{H}_5$, $(\text{CH}_3)_3\text{C}_6\text{H}_3$, $(\text{CH}_3)_2\text{C}_6\text{H}_4$, $\text{CH}_3\text{OC}_6\text{H}_5$, $\text{CH}_3\text{C}_6\text{H}_5$, C_6H_6, ClC_6H_5, $\text{CO}_2\text{CH}_3\text{C}_6\text{H}_5$	$\rho = -3.39(\sigma_p)$ $\log(k/h_0) = \rho\sigma$	42
$(\eta^6\text{-XC}_6\text{H}_5)\text{M(CO)}_3 + {}^{14}\text{C}_6\text{H}_5\text{X} \rightarrow$ $(\eta^6\text{-}{}^{14}\text{C}_6\text{H}_5\text{X})\text{M(CO)}_3 + \text{XC}_6\text{H}_5$ M = Cr, Mo, or W; X = H, Cl, CH_3	$\log k/\sigma_p$	41
$(\eta^6\text{-XC}_6\text{H}_4\text{CH}_2\text{Cl})\text{Cr(CO)}_3/\text{SCN}^-$ X = 4-OCH_3, H, 4-CH_3, 3-OCH_3, 3-F	$\log k/\sigma$	44
$[(\eta^6\text{-XC}_6\text{H}_4\text{CH}_2\text{Cl})\text{Cr(CO)}_3] \xrightarrow{e^-}$ $[(\eta^6\text{-XC}_6\text{H}_4\text{CH}_2\text{Cl})\text{Cr(CO)}_3]^-$ X = 4-OCH_3, H, 4-CH_3, 3-OCH_3, 3-F	$E_{1/2}$ (V)/σ	55
$(\eta^6\text{-XC}_6\text{H}_4\text{C(CH}_3)_2\text{CH}_2\text{OSO}_2\text{CH}_3)\text{Cr(CO)}_3/$ $\text{CH}_3\text{CO}_2\text{H}$, CH_3CO_2^- X = H, 4-OCH_3, 4-CH_3, 3-CH_3	$\log k/\sigma^+$ $\rho = -0.78$	45

TABLE 1 (Continued)

Chemical system	Correlation	Ref.
$(\eta^6\text{-}XC_6H_4C{\equiv}CMR_3)Cr(CO)_3/OH^-$ X = 2-, 3- or 4-CH_3, OCH_3, Cl, CF_3, H M = Si, R = CH_3; M = Ge, R = C_2H_5	log k/σ, σ^0, σ^n $\rho = 0.96$ (M = Ge, R = C_2H_5)	46
$(\eta^6\text{-}XC_6H_5)Cr(CO)_2L$ L = maleic anhydride, X = 1,2,3,4,5,6-$(CH_3)_6$, H, 1,3,5-$(CH_3)_3$, 1-CH_3-4-$Si(CH_3)_3$, 1,4-$(CH_3)_2$, OCH_3, 1-NH_2-4-$Si(CH_3)_3$, 1-CH_3-4-CO_2CH_3, F, 1,4-$(CO_2CH_3)_2$	k_{CO} (mdyne A^{-1})/$\Sigma\sigma_p$ $\nu(C{=}O)$ (cm^{-1})/$\Sigma\sigma_p$	48
$(\eta^6\text{-}XC_6H_5)W(CO)_3 + 3\ P(OCH_3)_3 \rightarrow [P(OCH_3)_3]_3W(CO)_3 + XC_6H_5$ X = CH_3CO_2, H, CH_3, 1,3,6-$(CH_3)_3$, OCH_3, $N(CH_3)_2$	log $k_2/\nu(CO)$ (cm^{-1})	47
$(\eta^6\text{-}XC_6H_5)Cr(CO)_2L$ L = phthalazine, pyridazine X = 1,2,3,4,5,6-$(CH_3)_6$, 1,3,5-$(CH_3)_3$, 1,4-$(CH_3)_2$, H, 1-CH_3-4-CO_2CH_3, 1,4-CO_2CH_3	k_{CO} (mdyne A^{-1})/$\Sigma\sigma_p$	50
$[(\eta^6\text{-}XC_6H_5)(\eta^5\text{-}C_5H_5)Fe]^+$ X = NH_2CH_3, C_2H_5, OCH_3, $NHCOCH_3$, Cl, F, CN, H, CO_2H, $CO_2C_2H_5$, $CONH_2$, OC_6H_5	$\delta(^1H)$ (ppm)/σ^e	51
$[(\eta^6\text{-}4\text{-}XC_6H_4CH_3)(\eta^5\text{-}C_5H_5)Fe]^+$ X = NH_2, CH_3, H, $CO_2C_2H_5$, $NHCOCH_3$, Cl, F, CN, H, CO_2H, $CO_2C_2H_5$, $CONH_2$, OC_6H_5	$\delta(^1H)$ (ppm)/σ^e $E_{1/2}$ (V)/σ_p^0 $\rho = 0.52$ V (CH_3CN)	51 52
$[(\eta^6\text{-}XC_6H_5)_2Cr] \rightarrow [(\eta^6\text{-}XC_6H_5)_2Cr]^+ + e^-$ X = OCH_3, F, H, CF_3, 1-Cl-2, 5-$(CH_3)_2$, CH_3, C_6H_5, 1-CF_3-3,4-Cl_2, 1-Cl-2-CF_3, 1,4-$(CF_3)_2$	$E_{1/2}$ (V)/σ_p	53
$[(\eta^6\text{-}XC_6H_5)_2Cr] \xrightarrow{e^-} [(\eta^6\text{-}XC_6H_5)_2Cr]^-$ X = 1,2,6-$(CH_3)_3$, CH_3, 1,3,5-$(CH_3)_3$, C_6H_5	$E_{1/2}$ (V)/σ	54
$[(\eta^6\text{-}t\text{-}C_4H_9COC_6H_4X)Cr(CO)_3] \xrightarrow{e^-} [(\eta^6\text{-}t\text{-}C_4H_9COC_6H_4X)Cr(CO)_3]^-$ X = 4-OCH_3, 3-t-C_4H_9, 4-CH_3, H, 3-F	$E_{1/2}$ (V)/σ $\rho = 0.48$ V (DMF)	56
(arene)$Cr(\eta^6\text{-}C_6H_6)$ arene = C_6F_6, C_6F_5H, $C_6F_4H_2$, C_6H_6	$\delta(^{13}C)$ (ppm)/$\Sigma\sigma_m$ $\delta(^1H)$ (ppm)/$\Sigma\sigma_m$	57
(arene)$Cr(CO)_3$ arene = 1,2,6-$C_6H_3(N(CH_3)_2)_3$, C_6H_5Cl, $C_6H_5N(CH_3)_2$, 2-$CH_3C_6H_4NH_2$, $C_6H_5NH_2$, 1,3,5-$(CH_3)_3C_6H_3$, 1,4-$(CH_3)_2C_6H_4$, 1,2-$(CH_3)_2C_6H_4$, $C_6H_5CH_3$,	$\delta^{13}(CO)/k_{CO}$ (mdyne A^{-1})	30

TABLE 1 (Continued)

Chemical system	Correlation	Ref.
$C_6H_5OCH_3$, C_6H_6, 1,3-$CH_3CO_2C_6H_4CH_3$, $C_6H_5CO_2CH_3$, 1,2-$Cl_2C_6H_4$		
(arene)$Cr(CO)_2(CS)$ arene = 1,2-$(CH_3)_2C_6H_3$, $C_6H_5CH_3$, $C_6H_5OCH_3$, C_6H_6, C_6H_5Cl, 1,3- $CH_3CO_2C_6H_4CH_3$, $C_6H_5CO_2CH_3$	$\delta(^{13}CO)/k_{CO}$ (mdyne $Å^{-1}$)	30

[a] $\Delta K(CO) = k_{CO}(H) - k_{CO}(X)$. [b] $\Delta S(m\text{-}X) = S^c(m\text{-}X) - S^f(m\text{-}X)$. [c] D_i = energy required to dissociate one CO ligand. [d] $\Delta pK_{BH^+} = pK_{BH^+}(\text{free}) - pK_{BH^+}(\text{complexed})$. [e] A combination of Hammett and Taft parameters.

the rings' σ-framework in the metal—arene bonds. In a related study, an attempt to correlate $E_{1/2}$ for the first reduction of some (arene)$_2$Cr complexes (arene = C_6H_6, $(C_6H_5)_2$, 1,2,6-$(CH_3)_3C_6H_3$ or 1,2-$(CH_3)_2C_6H_4$) in DMF with Taft's σ parameter has been briefly reported [54]. Reduction potentials for $(\eta^6\text{-}XC_6H_4COC(CH_3)_3)Cr(CO)_3$, $(\eta^6\text{-}XC_6H_4CH_2Cl)Cr(CO)_3$ and $(\eta^6\text{-}XC_6H_4CO_2CH_3)Cr(CO)_3$ have been recorded in DMF and the correlations between $E_{1/2}$ and σ discussed [55,56].

The ^{13}C and ^1H NMR chemical shifts of a number of closely related bis(arene)chromium(0) complexes have been recently shown to correlate with the quantity $\Sigma\sigma_m$ and it has also been suggested that this particular quantity can be used as an indicator of the "oxidative stability" for (arene)$_2$Cr and (arene)$Cr(\eta^6\text{-}C_6H_6)$ derivatives [57].

The foregoing data are summarized in Table 1.

(ii) Complexes containing a monohapto bonded phenyl ring

^1H NMR chemical shift data for the complexes, $(\eta^1\text{-}XC_6H_4)_2Ti(\eta^5\text{-}C_5H_5)_2$ have been correlated to Hammett and Taft σ parameters [58]. Plots of $\delta^{H}_{C_5H_5}$ versus the Hammett σ constants as well as a combination of the Taft parameters, σ_I and σ_R, were linear and the chemical shifts increased as X became more electron-withdrawing. The average shift of the *o*- and *m*-protons of a substituted derivative relative to the single resonance of $(\eta^1\text{-}C_6H_5)Ti(\eta^5\text{-}C_5H_5)$ was also plotted against σ or a combination of σ_I and σ_R to yield straight lines which were discussed in terms of their correlational acceptability. A brief report [59] has pointed out that the position of the characteristic absorption band (650—700 nm) for $(\eta^1\text{-}4\text{-}XC_6H_4)TiCl_2 \cdot 3$ pyridine adducts correlates with Hammett's σ_p parameter and that the ESR $\bar{g}$ values for these complexes exhibited a poor correlation with this parameter but a better correlation with Taft's σ_R parameter. However, the precise reasons for these observations are not clear.

Substituent effects in complexes of the type, $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_6H_4X)$ have been the subject of several reports [60—63]. The symmetric and asymmetric $\nu(CO)$ frequencies have been reported to show linear correlations with Taft's σ_I parameter [60] as well as Hammett's σ parameter [61]. In addition, the chemical shifts for the cyclopentadienyl protons correlate with σ. However, the changes observed for the $\nu(CO)$ frequencies and chemical shifts are small suggesting that there is little conjugation between the substituent X and the CO and C_5H_5 ligands. In contrast to these particular iron complexes, the three $\nu(CO)$ frequencies in $Mn(CO)_5(\eta^1\text{-}C_6H_4X)$ derivatives [64] are insensitive to the nature of X. This difference could be due in part to the fact that the electronic effect of X is transmitted to five CO groups rather than two.

The reactivity of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_6H_4X)$ derivatives towards $HgCl_2$ and SO_2 has been studied by Wojcicki and co-workers [62,63]. The rate of electrophilic attack of $HgCl_2$ [62] increases as X becomes more electron attracting and a reaction constant $\rho = -1.19$ was obtained from the slope of a plot of log k_2 versus σ^+ which is typical of an electrophilic aromatic substitution reaction [65].

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_6H_4X) + HgCl_2 \rightarrow (\eta^1\text{-}XC_6H_4)HgCl + (\eta^5\text{-}C_5H_5)Fe(CO)_2Cl \qquad (11)$$

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_6H_4X) + SO_2(l) \rightarrow (\eta^5\text{-}C_5H_5)Fe(CO)_2(SO_2C_6H_4X) \qquad (12)$$

The corresponding reaction constant for the insertion of SO_2 was -4.3 indicating that the reaction with $HgCl_2$ is much more sensitive to the nature of X than the reaction involving SO_2 [63].

Although ^1H NMR data for the ring protons in the complexes $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\eta^1\text{-}C_6H_4\text{-}4\text{-}X)$ could not be correlated to the nature of X [66], the reduction potential, $E_{1/2}(V)$, for the irreversible addition of one electron could be correlated to σ_p^0 according to eqn. (13) [63].

$$E_{1/2} = 0.19\,\sigma_p^0 - 2.01 \qquad (13)$$

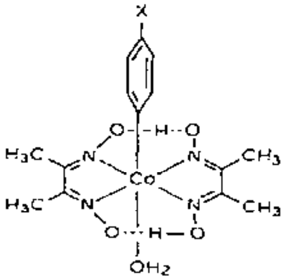
The electronic effect of a substituent on a phenyl ring in an axial position of $(\eta^1\text{-}4\text{-}XC_6H_4)Co(DH)_2(H_2O)$ derivatives, VIII, has been studied [67,68]. The rate of arylation of Hg(II)

$$(\eta^1\text{-}XC_6H_4)Co(DH)_2(H_2O) + Hg^{2+} + H_2O \rightarrow (\eta^1\text{-}XC_6H_4)Hg^+ + Co(DH)_2(H_2O)_2^+ \qquad (14)$$

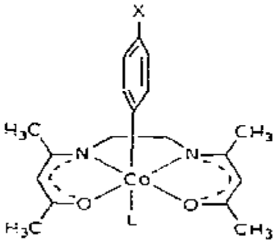
is enhanced as X becomes more electron donating and exhibits a large negative reaction constant, $\rho = -6.3$ [67]. A linear free energy relationship for the redox couple $[(\eta^1\text{-}4\text{-}XC_6H_4)Co(DH)_2(H_2O)]/[(\eta^1\text{-}4\text{-}XC_6H_4)Co(DH)_2(H_2O)]^+$ has also been reported [68] which has been interpreted in terms of the cobalt—arene bonding electrons being involved in the electron transfer process.

Chemical shift data in $CDCl_3$ for the methine hydrogens of IX have been used to calculate the formation constants for the equilibrium

$$(\eta^1\text{-}4\text{-}XC_6H_4)(bae)Co + L \rightleftharpoons (\eta^1\text{-}4\text{-}XC_6H_4)(bae)CoL \qquad (15)$$



VIII



IX

where L = pyridine-d_5 or piperidine and X = OCH_3, H, I, Br, CN or NO_2.

The formation constants are linearly related to the σ_p parameter indicating that the electronic effect of X on the axial phenyl ring is transmitted to the methine hydrogens via an inductive mechanism. The cobalt center becomes a stronger Lewis acid with respect to the other axial ligand, L, as X becomes more electron-withdrawing and this manifests itself in an increase in the magnitude of the formation constant [69]. A similar trend has also been reported recently with *o*-dichlorobenzene as solvent [70].

It has been qualitatively observed that aryl chlorides substituted with electron-donating groups are unreactive towards $Pd(PPh_3)_4$ but become activated with the introduction of electron withdrawing substituents. Consequently, the C—Cl bond in 4-XC_6H_4Cl (X = NO_2, CN, C_6H_5CO or H) is oxidatively cleaved by reaction with $Pd(PPh_3)_4$ to form $PdCl(\eta^1\text{-}4\text{-}XC_6H_4)(PPh_3)_2$ [71]. Foà and Cassar [72] have quantitatively studied the addition of aryl chlorides to the analogous nickel complex, $Ni(PPh_3)_4$, and have correlated the relative rates of oxidative-addition with the Hammett σ parameter

$$XC_6H_4Cl + Ni(PPh_3)_4 \rightarrow \textit{trans}\text{-}[NiCl(\eta^1\text{-}XC_6H_4)(PPh_3)_2] + 2\ PPh_3 \qquad (16)$$

For substituents having $\sigma > 0.23$ (4-C_6H_5O, 4-OCH_3, 4-CH_3, 3-CH_3) the Hammett plot yielded a large positive ρ value of 8.8, whereas for substituents having $\sigma < 0.23$ (4-Cl, 3-C_6H_5O, 3-Cl, 3-CO_2CH_3, 4-$COCH_3$, 3-CN, 4-C_6H_5CO, 4-CN) the substituent effect was minimal ($\rho \sim 0$). A mechanism which is consistent with these observations was proposed by these workers.

The relative rates of carbonylation of a number of substituted bromobenzenes catalyzed by $Ni(CO)_4$ in the presence of water have also been correlated with the σ parameters [73]. The rate of carbonylation increases as the substituent becomes more electron-attracting which is consistent with the notion that the reaction involves an initial nucleophilic attack by Ni at the C—Br bond followed in succession by CO insertion and reductive elimination to form the substituted benzoic acid.

Thermal stabilities have been used to study the effect of substituents associated with $Ni(Y)(\eta^1\text{-}XC_6H_4)(PPh_3)_2$ complexes where Y = Cl or Br and X = 2-CH_3, 4-Cl, H, 4-CH_3 or 3-CH_3 [74].

The effect of X in a number of complexes having a Pt—C_6H_4X moiety has

TABLE 2

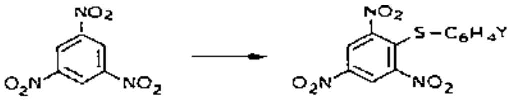
Summary of correlations involving monohapto bonded substituted phenyl rings

Chemical system	Correlation	Ref.
$(\eta^1\text{-XC}_6\text{H}_4)_2\text{Ti}(\eta^5\text{C}_5\text{H}_5)_2$ X = 4-$\text{N(CH}_3)_2$, 4-OCH_3, 4-CH_3, H, 4-F, 4-Cl, 4-Br, 4-CF_3, 3-CH_3, 3-CF_3	$\delta^{\text{H}}_{\text{C}_5\text{H}_5}$ (ppm)/σ, σ_I, σ_R $\delta^{\text{H}}_{\text{C}_6\text{H}_4}$ (ppm)/σ, σ_I, σ_R	58
$(\eta^1\text{-4-XC}_6\text{H}_4)\text{TiCl}_2\cdot 3\,\text{py}$ X = Cl, H, OC_6H_5, CH_3, OCH_3	$\bar{\nu}$ (cm^{-1})/σ $\bar{g}$ (gauss)/σ_R	59
$(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2(\eta^1\text{-C}_6\text{H}_4\text{X})$		
X = 4-Cl, 4-CH_3, H, 2,3,4,5,6-F_6	ν(CO) (cm^{-1})/σ_I	60
X = 3-OCH_3, 4-CH_3, 4-F, 4-Cl, 4-CO_2CH_3, 4-CN, 4-OCH_3,	ν(CO) (cm^{-1})/σ	61
$(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2(\eta^1\text{-C}_6\text{H}_4\text{X})/\text{HgCl}_2$ X = H, 4-OCH_3, 4-Cl	log k/σ^+ $\rho = -1.19$ (THF)	62
$(\eta^1\text{-C}_5\text{H}_5)\text{Fe(CO)}_2(\eta^1\text{-C}_6\text{H}_4\text{X})/\text{SO}_2\text{(l)}$ X = 4-OCH_3, 2-CH_3, 4-CH_3, H, 3-CH_3	log k/σ^+ $\rho = -4.3$	63
$(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)(PPh}_3)(\eta^1\text{-C}_6\text{H}_4\text{X})$ X = 4-OCH_3, 4-CH_3, H, 4-F, 4-Cl, 4-$\text{CO}_2\text{C}_2\text{H}_5$	$E_{1/2}$ (V)/σ_p^0 $\rho = -0.19$ (CH_3CN)	60
$(\eta^1\text{-4-XC}_6\text{H}_4)\text{Co(DH)}_2(\text{H}_2\text{O})/\text{Hg}^{2+}$ X = H, F, CH_3, OCH_3	log k/σ $\rho = -6.3$	67
$(\eta^1\text{-4-XC}_6\text{H}_4)\text{Co(DH)}_2(\text{H}_2\text{O})/(\eta^1\text{-4-XC}_6\text{H}_4)\text{Co(DH)}_2(\text{H}_2\text{O})^+$ X = F, Cl, Br, H, CH_3, OCH_3	$E_{1/2}$ (V)/σ^+ $\rho > 0$ (1.0 M HClO_4)	68
$(\eta^1\text{-4-XC}_6\text{H}_4)(\text{bae})\text{Co} + \text{L} \rightleftharpoons (\eta^1\text{-4-XC}_6\text{H}_4)(\text{bae})\text{CoL}$ L = pyridine; X = OCH_3, H, I, Br, CN, NO_2 L = piperidine; X = H, I, Br, CN, NO_2	K/σ_p	69
$\text{Ni(PPh}_3)_4 + \text{XC}_6\text{H}_4\text{Cl} \rightarrow \text{NiCl}(\eta^1\text{-XC}_6\text{H}_4)(\text{PPh}_3)_2 + 2\,\text{PPh}_3$ X = 4-OC_6H_5, 4-OCH_3, 4-CH_3, 3-CH_3, H, 4-Cl, 3-OC_6H_5, 3-Cl, 3-CO_2CH_3, 4-COCH_3, 3-CN, 4-COC_6H_5, 4-CN	log k/σ $\rho = 8.8$ for $\sigma > 0.23$ (benzene) $\rho \sim 0$ for $\sigma < 0.23$ (benzene)	72
$\text{XC}_6\text{H}_4\text{Br} + \text{CO} + \text{H}_2\text{O} \xrightarrow{\text{Ni(CO)}_4} \text{XC}_6\text{H}_4\text{CO}_2\text{H} + \text{HBr}$ X = H, 4-OCH_3, 4-NHCOCH_3, 4-CH_3, 4-CH=CH_2, 4-Cl, 4-COCH_3, 4-CN, 3-CH=CH_2, 3-CH_3, 3-Cl, 3-CN, 2-CH_3, 2-OCH_3, 2-$(\text{CH})_4$, 2-Cl, 2-NHCOCH_3, 2,4,6-$(\text{CH}_3)_3$	log rel. rate/σ $\rho = 2.7$ (DMSO)	73

TABLE 2 (Continued)

Chemical system	Correlation	Ref.
cis-$[Pt(\eta^1\text{-}C_6H_4X)_2(P(C_2H_5)_3)_2] + H^+ + Cl^- \rightarrow$ *cis*-$[Pt(\eta^1\text{-}C_6H_4X)(Cl)(P(C_2H_5)_3)_2] + C_6H_5X$ X = 4-$N(CH_3)_2$, 4-CH_3, 4-OCH_3, H, 3-OCH_3, 4-F, 4-Cl, 3-F, 2-CH_3, 2-C_2H_5, 3-CF_3	$\log k/\sigma$ $\rho = -5.1$ (MeOH) $\rho = -4.5$ (10% aq. MeOH)	77
$[Pt(\eta^1\text{-}C_6H_4X)_2(P(C_2H_5)_3)_2]/[Pt(\eta^1\text{-}C_6H_4X)_2(P(C_2H_5)_3)_2]^+$ X = 4-OCH_3, 4-CH_3, H, 4-Cl, 4-F, 3-CF_3	$(E_p)_A/\sigma$	72
trans-$[Pt(PEt_3)_2(C_6H_4X)(CH_3)] + H^+ + Cl^- \rightarrow$ *trans*-$[Pt(\eta^1 C_6H_4X)(PEt_3)_2Cl] + CH_4$ X = H, 3-CH_3, 2-CH_3, 3-F, 4-F, 3-CF_3, 2,3,4,5,6-F_5	$\log k/\sigma$	81
trans-$[PtI(\eta^1\text{-}XC_6H_4)(PAr_3)_2] + CO \rightarrow$ *trans*-$[PtI(COC_6H_4X)(PAr_3)_2]$ Ar = C_6H_5 or 4-$CH_3C_6H_4$	$\log k_2/\sigma$ $\rho = -3.6$ ($C_2H_2Cl_4$)	79
X = 4-Cl, H, 4-CH_3, 4-OCH_3, 2-OCH_3, 2-CO_2CH_3	$\log k_2/\sigma^+$ $\rho = -0.29$ ($C_2H_2Cl_4$)	78
cis-$[Pt(\eta^1\text{-}C_6H_4X)_2(PPh_3)_2]$ *cis*-$[Pt(\eta^1\text{-}C_6H_4X)_2(Ph_2C_2H_4Ph_2)]$ X = 4-NO_2, 4-Br, 4-Cl, 4-OCH_3, 4-SCH_3, H, 4-$Si(CH_3)_3$, 4-CH_3	$^1J(Pt\text{—}P)$ (Hz)/σ_I	82
cis-$[Pt(bipy)(\eta^1\text{-}C_6H_4X)_2]$ X = 2-OCH_3, 4-CH_3, 2-CH_3, H, 4-Cl, 4-F, 3-F	$\tilde{\nu}_{CT}$ (cm^{-1})/σ	87, 86
cis-$[Pt(bipy)(\eta^1\text{-}C_6H_4X)_2] + CH_3I \rightarrow [Pt(CH_3)(I)(\eta^1\text{-}C_6H_4X)_2(bipy)]$ X = 4-OCH_3, 4-CH_3, H, 4-F, 4-Cl, 3-OCH_3	$\log k/\sigma$ $\quad\sigma$, LMCT $\rho = 2.6$ (acetone)	88
trans-$[Pt(\eta^1\text{-}(C_6H_4X)(Y)(P(C_2H_5)_3)_2$ X = H, 3-F, 4-F Y = F_2H, F, Cl, Br, I, CH_3, CH_2, C_6H_5, $CH{=}CH_2$, $CH{=}C(CH_3)_2$, OCH_3, SC_2H_5, N_3, NO_2, NCO, $SnCl_3$	$\delta(^{13}C)$ (ppm)/Taft, Swain-Lupton constants $^2J(Pt\text{—}C)$ (Hz)/Taft, Swain-Lupton constants $^3J(Pt\text{—}C)$ (Hz)/Taft, Swain-Lupton constants	88
$(\eta^1\text{-}XC_6H_4)HgCl + HCl \rightarrow XC_6H_5 + HgCl_2$ X = H, 4-CH_3, 3-CH_3, 4-Cl, 3-Cl, 4-OCH_3, 3-OCH_3	$\log k/\sigma^+$ $\rho = -2.4$ (aq. ethanol)	93
cis-$[Pt(\eta^4\text{-}1,3\text{-}C_8H_{12})(\eta^1\text{-}C_6H_4X)_2]$ X = 4-OCH_3, 4-CH_3, 3-CH_3, H, 4-Cl, 3-Cl, 3-CF_3	$J(Pt\text{—}C)$ (Hz)/σ^0	86

TABLE 2 (Continued)

Chemical system	Correlation	Ref.
$(\eta^1\text{-}XC_6H_4)HgBr + HCl \rightarrow XC_6H_5 + HgBrCl$ X = 4-OCH_3, 4-CH_3, 3-CH_3, H, 4-Cl, 4-CO_2CH_3	$\log k/\sigma^+$ $\rho = -1.77$ (DMF)	94
$(\eta^1\text{-}XC_6H_4)_2Hg + HCl \rightarrow XC_6H_5 + (\eta^1\text{-}XC_6H_4)HgCl$ X = 4-OCH_3, 4-Cl, 4-F, 4-C_6H_5, 3-NO_2, H	$\log k/(\sigma + \sigma^+)/2$ $\rho = -2.8$ (DMSO/dioxane)	95
$(\eta^1\text{-}XC_6H_4)_2Hg + HgI_2 \rightarrow 2(\eta^1\text{-}XC_6H_4)HgI$ X = 4-OCH_3, 4-CH_3, 4-Cl, 4-F, 4-C_6H_5, H	$\log k/\sigma$ $\rho = -5.9$ (dioxane)	96
$(\eta^1\text{-}XC_6H_4)_2Hg + {}^{203}Hg(I) \rightarrow Hg(I) + (\eta^1\text{-}XC_6H_4)_2{}^{203}Hg$ X = H, 4-CH_3, 4-OCH_3, 3-CH_3, 4-Cl, 3-Cl	$\log k/(\sigma + \sigma^+)/2$ $\rho = -1.0$	97
$(\eta^1\text{-}XC_6H_4)_2TlCl + Hg \rightarrow TlCl + (\eta^1\text{-}XC_6H_4)_2Hg$ X = 4-OCH_3, 4-CH_3, 3-CH_3, H, 4-Cl, 4-CO_2CH_3	$\log k/\sigma^+$ $\rho = -2.83$ (DMF)	98
$(\eta^1\text{-}XC_6H_4)HgSC_6H_4Y$ +  + $(\eta^1\text{-}XC_6H_4)HgI$	$\log k/\sigma$	101
Y = H; X = 4-CH_3, 3-CH_3, H, 4-Cl, 3-Cl, 2-CH_3, 2,4,6-$(CH_3)_3$	$\rho = -0.98$ (benzene)	
X = H; Y = 4-CH_3, 3-CH_3, H, 4-Cl, 3-Cl, 2-CH_3, 2,4,6-$(CH_3)_3$	$\rho = -3.7$ (benzene)	
$XC_6H_4Cl + NaCN \xrightarrow{NiCl(C_7H_{10})(PPh_3)_2,\ PPh_3} XC_6H_4CN + NaCl$ X = 4-CH_3, 4-OCH_3, 4-OC_6H_5, 3-CH_3 4-C_6H_5, H, 4-F, 3-OC_6H_5, 3-CO_2CH_3, 4-$COCH_3$, 4-CN	$\log k/\sigma$ $\rho = 4.8$ (ethanol)	102

been studied [75—84,86—89]. The relative rates of reaction for

$$trans\text{-}Pt(\eta^1\text{-}C_6H_4X)Cl(PEt_3)_2 + py \rightarrow trans\text{-}Pt(\eta^1\text{-}C_6H_4X)(py)(PEt_3)_2{}^+ + Cl^- \quad (17)$$

were found to be rather insensitive to the nature of X [75] which was taken to be support for an inductive mechanism for the *trans*-effect [90]. More recent kinetic studies have involved electrophilic attack by HCl [76,77] and carbonylation [78,79] at the Pt—C bond of the Pt—C_6H_4X moiety. The

Hammett correlation for

$$\textit{cis}\text{-}[\mathrm{Pt}(\eta^1\text{-}\mathrm{C_6H_4X})_2(\mathrm{PEt_3})_2] + \mathrm{H^+} + \mathrm{Cl^-} \rightarrow \textit{cis}\text{-}[\mathrm{Pt}(\eta^1\text{-}\mathrm{C_6H_4X})(\mathrm{Cl})(\mathrm{PEt_3})_2] + \mathrm{C_6H_5X} \tag{18}$$

yielded a reaction constant of about —5.0 (see Table 2) which has been used to support a proposed mechanism [77]. The anodic peak potential, $(E_p)_A$, for *cis*-$\mathrm{Pt}(\eta^1\text{-}\mathrm{C_6H_4X})_2(\mathrm{PEt_3})_2$ has also been correlated to σ and increases linearly with increasing electron withdrawing ability of X [80] as a result of the decreased electron density at the metal center. This parallels the variation in rate of electrophilic attack by HCl noted previously. In a recent communication a satisfactory Hammett correlation has also been reported for the electrophilic addition of HCl to *trans*-$[\mathrm{Pt}(\mathrm{PEt_3})_2(\eta^1\text{-}\mathrm{C_6H_4X})(\mathrm{CH_3})]$ [81].

$$\textit{trans}\text{-}[\mathrm{Pt}(\mathrm{PEt_3})_2(\eta^1\text{-}\mathrm{C_6H_4X})(\mathrm{CH_3})] + \mathrm{H^+} + \mathrm{Cl^-} \rightarrow \textit{trans}\text{-}[\mathrm{Pt}(\eta^1\text{-}\mathrm{C_6H_4X})(\mathrm{PEt_3})_2\mathrm{Cl}] + \mathrm{CH_4} \tag{19}$$

The rate of reaction decreases and X becomes more electron withdrawing.

The following mechanism has been proposed for the addition of CO to *trans*-$\mathrm{PtI}(\eta^1\text{-}\mathrm{C_6H_4X})(\mathrm{PAr_3})_2$

$$\begin{tikzcd}
\mathrm{PtI}(\eta^1\text{-}\mathrm{C_6H_4X})(\mathrm{PAr_3})_2 + \mathrm{CO} \arrow[r, shift left, "K_1"] & \mathrm{PtI}(\eta^1\text{-}\mathrm{C_6H_4X})(\mathrm{CO})(\mathrm{PAr_3})_2 \arrow[l, shift left] \arrow[r, shift left, "k_3 - \mathrm{PAr_3}"] \arrow[d, "k_2"] & \mathrm{PtI}(\eta^1\text{-}\mathrm{C_6H_4X})(\mathrm{CO})(\mathrm{PAr_3}) \arrow[l, shift left, "k_3 + \mathrm{PAr_3}"] \arrow[d, "k_4"] \\
 & \mathrm{PtI}(\mathrm{COC_6H_4X})(\mathrm{PAr_3})_2 & \mathrm{PtI}(\mathrm{COC_6H_4X})(\mathrm{PAr_3}) \arrow[l, "k_5", "+\mathrm{PAr_3}"']
\end{tikzcd}$$

and it was noted that a plot of log k_2 versus σ^+ gave $\rho = -0.29$ [78] whereas a plot of log Kk_2 versus σ gave $\rho = -3.6$ [79]. These reaction constants illustrate the difficulty encountered in attempting to rationalize the capricious nature of ρ values in organometallic systems [91].

The coupling constant ${}^1J(\mathrm{Pt{-}P})$ increases as X becomes more electron withdrawing in the complexes, *cis*-$\mathrm{Pt}(\eta^1\text{-}\mathrm{C_6H_4X})_2(\mathrm{PPh_3})_2$ and *cis*-$\mathrm{Pt}(\mathrm{Ph_2PC_2H_4PPh_2})(\eta^1\text{-}\mathrm{C_6H_4X})_2$ and show a good correlation with σ_I but not σ_p or σ_p^0 [82]. Such a correlation is in accord with the *trans*-influence theory [92] and the notion that the magnitude of *s*-electron density in the Pt—P bonds will increase with decreasing σ-electron density on the bonded carbon of the *trans*-ligand [90]. It is interesting to note however that the ^{31}P chemical shifts are insensitive to the nature of X. A similar observation has recently been reported for *trans*-$[\mathrm{Pt}(\mathrm{CH_3})(\mathrm{XC_5H_4N})(\mathrm{Ph_2PC_2H_4PPh_2})]$ [83] (X = 4-$\mathrm{N(CH_3)_2}$, 4-$\mathrm{CH_3}$, H, 4-$\mathrm{CO_2CH_3}$, 4-$\mathrm{COCH_3}$ or 4-CN) for which $J(\mathrm{Pt{-}P})$ shows a correlation with σ but the ^{31}P chemical shift for the P atom *trans* to the substituted pyridine does not. The nature of the metal may play a role in determining whether or not a successful correlation is observed since a linear correlation exists between the ^{31}P chemical shifts and σ for the analogous palladium complexes, *trans*-$[Pd(CH_3)(XC_5H_4N)(Ph_2C_2H_4PPh_2)$ [83].

For *cis*-$Pt(\eta^4\text{-}1,3\text{-}C_8H_{12})(\eta^1\text{-}C_6H_4X)_2$ complexes (X = 4-Cl, 4-C_6H_5, 4-CH_3, 4-F, 3-F, 2-CH_3) the ^{195}Pt chemical shifts are also invariant to the nature of X which suggests that electronic changes at platinum due to a change in X are minimal in these complexes [84]. The chemical shifts of the olefinic protons are also insensitive to the nature of X [82]. In contrast however, the chemical shifts of the olefinic carbon atoms increase as X becomes more electron-withdrawing and show an excellent correlation with the parameter, σ^0 [85] and a somewhat poorer correlation with the normal Hammett parameter, σ, a result which is in keeping with the notion that there is not extended π-interaction between the substituent and the olefinic carbon atoms [86].

On the other hand the position of the metal ligand charge transfer bands (MLCT) for $Pt(bipy)(\eta^1\text{-}C_6H_4X)_2$ complexes has been correlated to Hammett's σ parameter [87] as well as the σ^0 parameter [86]. This has also been related to the ability of these complexes to oxidatively add methyl iodide [88]. The good correlation between the first low energy LMCT band and log k_2 for the oxidative addition has been taken to be a reflection of the fact that oxidative addition is primarily dependent on the energy of the filled Pt(II) *d*-orbitals in these complexes. Those complexes having X = 4-CF_3 or 2-CH_3 failed to react, presumably because of an electronic and steric effect respectively.

The ^{13}C chemical shifts and $^{195}Pt—^{13}C$ coupling constants in complexes of the type, *trans*-$Pt(\eta^1\text{-}C_6H_4X)(Y)(PEt_3)_2$ (X = H, 3-F, 4-F; Y = an anionic ligand) have also been subjected to a detailed correlational analysis involving sets of both Taft and modified Swain-Lupton parameters [89].

Substituent effects associated with aryl and diarylmercury(II) derivatives have been studied from several points of view [93—99]. The rates of reaction for

$$(\eta^1\text{-}XC_6H_4)HgCl + HCl \rightarrow XC_6H_5 + HgCl_2 \qquad (20)$$

$$(\eta^1\text{-}XC_6H_4)HgBr + HCl \rightarrow XC_6H_5 + HgBrCl \qquad (21)$$

$$(\eta^1\text{-}XC_6H_4)_2Hg + HCl \rightarrow XC_6H_5 + (\eta^1\text{-}XC_6H_4)HgCl \qquad (22)$$

have been correlated to σ^+ (ρ = —2.4, —1.77) and $(\sigma + \sigma^+)/2$ (ρ = —2.8) respectively [93—95]. Electron withdrawing substituents cause a decrease in the rates of these reactions and vice versa for electron releasing substituents which is consistent with an electrophilic attack at Hg by HCl. A similar correlation (log k versus σ, ρ = —5.87) has been observed for eqn. (23) [96]. The rate of the exchange reaction, eqn. (24), has been studied as a function of X and the best correlation obtained with σ (ρ = —1.0) rather than σ^+ or $(\sigma + \sigma^+)/2$ [97].

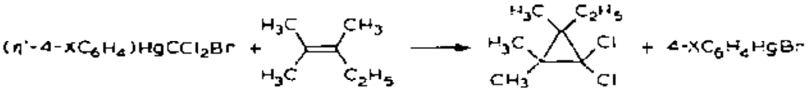
$$(\eta^1\text{-}XC_6H_4)_2Hg + HgI_2 \rightarrow 2(\eta^1\text{-}XC_6H_4)HgI \qquad (23)$$

$$(\eta^1\text{-}XC_6H_4)_2Hg + {}^{203}Hg(l) \rightarrow Hg(l) + (\eta^1\text{-}XC_6H_4)_2^{203}Hg \qquad (24)$$

$$(\eta^1\text{-XC}_6\text{H}_4)_2\text{TlCl} + \text{Hg} \xrightarrow{\text{DMF}} (\eta^1\text{-XC}_6\text{H}_4)_2\text{Hg} + \text{TlCl} \qquad (25)$$

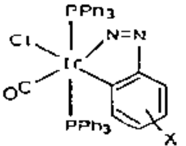
Polarography at a dropping mercury electrode was used to study reaction (25) [98].

The reactivity of $(\eta^1\text{-4-XC}_6\text{H}_4)\text{HgCCl}_2\text{Br}$ towards $(\text{CH}_3)_2\text{C=C(CH}_3)(\text{C}_2\text{H}_5)$ has been studied [99]. Variations in the nature of X exerted no pronounced effect on the reaction, which is consistent with the reaction proceeding via a concerted extrusion of CCl_2 from the aryl mercury compound (X = H, Cl, F, CH_3 or OCH_3).



(26)

The fact that there is no correlation between ν(CO) and the Hammett σ parameters for X (X = H, 4-CF_3, 3-OCH_3, one of 3- or 4-F, Cl, Br, CH_3, or NO_2) in the complexes, $\text{IrCl(N}_2\text{C}_6\text{H}_3\text{X)(CO)(PPh}_3)_2$ lends support to the proposed structure, IX, in which the *o*-metallated phenyl ring is *trans* to Cl rather than CO [100].



X

The rate of reaction (27) is enhanced as the substituents X or Y

$$(\eta^1\text{-XC}_6\text{H}_4)\text{HgSC}_6\text{H}_4\text{Y} + 2,4,6\text{-(NO}_2)_3\text{C}_6\text{H}_2\text{I} \rightarrow 2,4,6\text{-(NO}_2)_3\text{C}_6\text{H}_2\text{SC}_6\text{H}_4\text{Y}$$
$$+ (\eta^1\text{-XC}_6\text{H}_4)\text{HgI} \qquad (27)$$

become more electron releasing [101]. Hammett plots yielded $\rho = -0.98$ for Y = H and X = 4-CH_3, 3-CH_3, H, 4-Cl, 3-Cl, 2-CH_3, or 2,4,6-$(\text{CH}_3)_3$ and $\rho = -3.7$ for X = H and Y = 4-CH_3, 3-CH_3, H, 4-Cl, 3-Cl, 2-CH_3, or 2,4,6-$(\text{CH}_3)_3$ which are consistent with a four centered transition state.

The relative rate of cyanation of aryl halides in the presence of a nickel complex as catalyst

$$\text{XC}_6\text{H}_4\text{Cl} + \text{NaCN} \xrightarrow{\text{NiCl(C}_7\text{H}_{10})(\text{PPh}_3)_2,\ \text{PPh}_3} \text{XC}_6\text{H}_4\text{CN} + \text{NaCl} \qquad (28)$$

increases as X becomes more electron withdrawing [102] and has been plotted versus Hammett's σ parameter. The resulting Hammett plot is similar to that obtained for data pertaining to the oxidative addition of aryl halides to $\text{Ni(PPh}_3)_4$ [72]. Table 2 provides a summary of the foregoing correlations.

C. COMPLEXES CONTAINING A REMOTE SUBSTITUTED PHENYL RING AND A METAL—CARBON BOND

(i) Benzyl complexes

The reactivity of organochromium(III) species containing a substituted benzyl group towards electrophilic reagents such as I_2, Br_2, Hg^{2+} and $(CH_3)Hg^+$ has been studied [103,104].

$$[(H_2O)_5Cr(CH_2C_6H_4X)]^{2+} + I_2 + H_2O \rightarrow [Cr(H_2O)_6]^{3+} + ICH_2C_6H_4X + I^- \quad (29)$$

$$[(H_2O)_5Cr(CH_2C_6H_4X)]^{2+} + Br_2 + H_2O \rightarrow [Cr(H_2O)_6]^{3+} + BrCH_2C_6H_4X + Br^- \quad (30)$$

$$[(H_2O)_5Cr(CH_2C_6H_4X)]^{2+} + Hg^{2+} + H_2O \rightarrow [Cr(H_2O)_6]^{3+} + (\eta^1\text{-}XC_6H_4CH_2)Hg^+ \quad (31)$$

$$[(H_2O)_5Cr(CH_2C_6H_4X)]^{2+} + CH_3Hg^+ + H_2O \rightarrow [Cr(H_2O)_6]^{3+} + (\eta^1\text{-}XC_6H_4CH_2)HgCH_3 \quad (32)$$

In accord with electrophilic reactions, plots of log k versus Hammett's σ parameter for X yielded negative reaction constants (see Table 3).

The electronic effect of a substituent on a benzyl group occupying an axial position in $(\eta^1\text{-}4\text{-}XC_6H_4CH_2)Co(DH)_2(H_2O)$ derivatives has also been reported [67,68,105,106]. The arylation of Hg(II)

$$(\eta^1\text{-}XC_6H_4CH_2)Co(DH)_2(H_2O) + Hg^{2+} + H_2O \rightarrow (\eta^1\text{-}XC_6H_4CH_2)Hg^+ + Co(DH)_2(H_2O)_2^+ \quad (33)$$

yielded a ρ value of approximately -1.2 from the Hammett plot of log k versus σ which is much smaller than the value of -6.3 observed for the analogous reaction involving an axial substituted phenyl group [67]. This difference presumably reflects the electronic insulating ability of a CH_2 group. A small reaction constant ($\rho \sim -1$) has also been reported for the exchange reaction (34) [107].

$$(\eta^1\text{-}XC_6H_4CH_2)HgBr + {}^{203}HgBr_2 \rightarrow (\eta^1\text{-}XC_6H_4CH_2)\,{}^{203}HgBr + HgBr_2 \quad (34)$$

However a large negative reaction constant ($\rho = -5.2$) has been noted for

$$[(\eta^1\text{-}XC_6H_4CH_2)Co(DH)_2(H_2O)] + IrCl_6^{2-} \rightarrow [(\eta^1\text{-}XC_6H_4CH_2)Co(DH)_2(H_2O)] + IrCl_6^{3-} \quad (35)$$

which has been interpreted in terms of the presence of a Co(III) metal center associated with the $XC_6H_4CH_2\cdot$ radical during the course of the reaction [105]. The unpredictable behaviour of ρ values in these systems is well illustrated by the redox couple, $[(\eta^1\text{-}4\text{-}XC_6H_4CH_2)Co(DH)_2(H_2O)]/[(\eta^1\text{-}4\text{-}XC_6H_4CH_2)Co(DH)_2(H_2O)]^+$ [68,106] for which ρ is negative but positive for the analogous phenyl derivatives (see Table 2). The precise reason for this is not known. It is also interesting to note at this point that the equilibrium constants for

$$[ArCo(DH)_2(H_2O)] + H^+ \rightleftharpoons [ArCo(DH_2)(DH)(H_2O)]^+ \qquad (36)$$

are essentially insensitive to the nature of X [67]. Apparently the oxygen atoms of the DH ligand are too far away to feel the full electronic impact of X on the axial aryl group (substituted phenyl or benzyl), Ar

Kinetic data for the reaction of a series of 4-substituted benzyl bromides with $Co(DH)_2(PPh_3)$ indicate that the rate of reaction increases as X becomes more electron withdrawing and give $\rho = 1.4$ from the Hammett plot [108]. This is consistent with electron transfer from cobalt(II) to the aryl halide in the transition state.

$$2\ Co(DH)_2(PPh_3) + 4\text{-}XC_6H_4CH_2Br \rightarrow BrCo(DH)_2(PPh_3)$$
$$+ (\eta^1\text{-}XC_6H_4CH_2)Co(DH)_2(PPh_3) \qquad (37)$$

The rate of oxidative addition of $4\text{-}XC_6H_4CH_2Cl$ (X = H, F, Cl, CH_3 or NO_2) to *trans*-$IrCl(CO)[PEt_nPh_{3-n}]_2$ (n = 0, 1 or 2) in benzene does not show a good linear correlation with the σ_p values of X [109]. This result differs from the rates of oxidative addition of $4\text{-}XC_6H_4CH_2Br$ to *trans*-IrCl(CO)$(PPh_3)_2$ in DMF which decrease in the order $CH_3 > Br > H > NO_2$ [110]. This difference has been attributed to the different solvents used [109].

The relative rates of the nickel catalyzed amination of several substituted benzyl bromides increases as the substituents become more electron withdrawing [111] which parallels the rates of the corresponding nickel catalyzed carbonylation [73].

Recently the decomposition of $(\eta^1\text{-}XC_6H_4CH_2)_2Hg$ complexes

$$(\eta^1\text{-}XC_6H_4CH_2)_2Hg \rightarrow XC_6H_4CH_2\cdot + (\eta^1\text{-}XC_6H_4CH_2)Hg\cdot \qquad (38)$$

$$(\eta^1\text{-}XC_6H_4CH_2)Hg\cdot \rightarrow Hg + XC_6H_4CH_2\cdot \qquad (39)$$

has been proposed as a model for quantifying substituent effects in free radical reactions. A set of $\sigma\cdot$ parameters were calculated from an extended Hammett equation

$$\log(k_1/k_0) = \rho\sigma + (\rho^\cdot)(\sigma^\cdot) \qquad (40)$$

where $\rho\cdot = 1$ for reactions (38) and (39) and $\sigma\cdot$ is the substituent constant for a *para*-substituent on a benzyl free radical [112].

The foregoing correlations are summarized in Table 3.

(ii) Benzoyl and phenylacetyl complexes

The cyclopentadienyl proton chemical shifts in a series of $(\eta^5\text{-}C_5H_5)$ $Mn(NO)(PPh_3)(COC_6H_4X)$ complexes show a linear correlation with Hammett's σ parameter [113] and shift downfield as X becomes more elec-

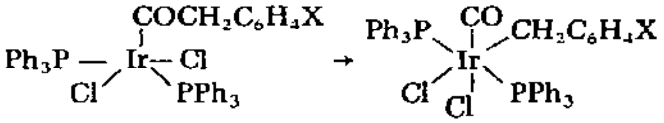
TABLE 3

Summary of correlations involving substituted benzyl complexes

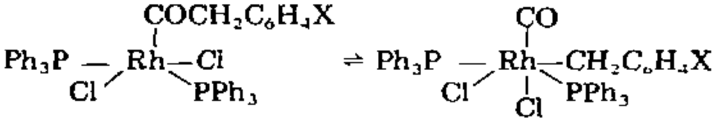
Chemical system	Correlation	Ref.
$[(H_2O)_5CrCH_2C_6H_4X]^{2+} + I_2 + H_2O \rightarrow [Cr(H_2O)_6]^{3+} +$ $ICH_2C_6H_4X + I^-$	$\log k/\sigma_p$ $\rho = -0.81$	103
$[(H_2O)_5CrCH_2C_6H_4X]^{2+} + Br_2 + H_2O \rightarrow [Cr(H_2O)_6]^{3+} +$ $BrCH_2C_6H_4X + Br^-$	$\log k/\sigma_p$ $\rho = -1.29$	103
$[(H_2O)_5CrCH_2C_6H_4X]^{2+} + Hg^{2+} + H_2O \rightarrow$ $[Cr(H_2O)_6]^{3+} + (\eta^1\text{-}XC_6H_4CH_2)Hg^+$	$\log k/\sigma$ $\rho = -0.62$	104
$[(H_2O)_5CrCH_2C_6H_4X]^{2+} + CH_3Hg^+ + H_2O \rightarrow$ $[Cr(H_2O)_6]^{3+} + (\eta^1\text{-}XC_6H_4CH_2)HgCH_3$ $X = 4\text{-}CH_3, H, 4\text{-}Br, 4\text{-}CF_3, 4\text{-}CN$	$\log k/\sigma$ $\rho = -0.85$	104
$[(\eta^1\text{-}XC_6H_4CH_2)Co(DH)_2(H_2O)] + Hg^{2+} + H_2O \rightarrow$ $XC_6H_4CH_2Hg^+ + Co(DH)_2(H_2O)_2{}^+$ $X = 4\text{-}F, H, 4\text{-}CH_3, 4\text{-}OCH_3$	$\log k/\sigma$ $\rho \sim -1.2$	67
$[(\eta^1\text{-}XC_6H_4CH_2)Co(DH)_2(H_2O)] + IrCl_6^{2-} \rightarrow$ $[(\eta^1\text{-}XC_6H_4CH_2)Co(DH)_2(H_2O)]^+ + IrCl_6^{3-}$ $X = 4\text{-}NO_2, 4\text{-}F, H, 4\text{-}CH_3, 4\text{-}OCH_3$	$\log k/\sigma$ $\rho = -5.2$	105
$[(\eta^1\text{-}XC_6H_4CH_2)Co(DH)_2(H_2O)]/[(\eta^1\text{-}XC_6H_4CH_2)Co\text{-}$ $(DH)_2(H_2O)]^+$ $X = 4\text{-}NO_2, 4\text{-}CN, 4\text{-}Br, 4\text{-}Cl, H, t\text{-}C_4H_9, 4\text{-}CH_3, 4\text{-}OCH_3$	$E_{1/2}$ (V)/σ^+ $\rho = -1.2$	68, 106
$2\ Co(DH)_2(PPh_3) + 4\text{-}XC_6H_4CH_2Br \rightarrow BrCo(DH)_2(PPh_3)$ $+ (\eta^1\text{-}4\text{-}XC_6H_4CH_2)Co(DH)_2(PPh_3)$ $X = H, CH_3, Br, CN, NO_2$	$\log k/\sigma$ $\rho = 1.4$ (benzene)	108
$(\eta^1\text{-}XC_6H_4CH_2)HgBr + {}^{203}HgBr \rightarrow$ $(\eta^1\text{-}XC_6H_4CH_2){}^{203}HgBr + HgBr_2$ $X = 4\text{-}CH_3, 4\text{-}i\text{-}C_3H_7, H, 4\text{-}F, 4\text{-}Cl$	$\log k/\sigma$ $\rho \sim -1$ (quinoline)	107
$(\eta^1\text{-}XC_6H_4CH_2)_2Hg \rightarrow XC_6H_4CH_2\cdot + (\eta^1\text{-}XC_6H_4CH_2)Hg\cdot$ $(\eta^1\text{-}XC_6H_4CH_2)Hg\cdot \rightarrow Hg + XC_6H_4CH_2\cdot$ $X = H, 3\text{-}F, 3\text{-}OCH_3, 3,5\text{-}(CH_3)_2, 4\text{-}Cl, 4\text{-}F, 4\text{-}OCH_3,$ $4\text{-}CH_3, 4\text{-}C_6H_5, 4\text{-}NO_2$	$\log k_1/\sigma$ $\rho = -0.6$ (octane)	112

tron releasing. However, there are no apparent correlations between the σ values for X and the ν(CO) and ν(NO) frequencies in the IR. These complexes have also been resolved into their respective enantiomers and the rate of racemization in toluene increases with the introduction of electron releasing substituents on the benzoyl ring ($\rho = -1.8$) [113].

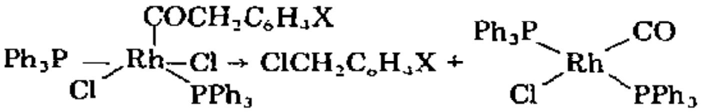
Kinetic data for the migration of the aryl group of a substituted benzoyl or phenylacetyl ligand coordinated to iridium [114] and rhodium [91] clearly illustrate the difficulty often encountered in ascertaining the significance of a Hammett correlation in organometallic systems. The rate of reactions (41) and (42) in the forward direction increases as X becomes



$$\mathrm{Ph_3P{-}\overset{COCH_2C_6H_4X}{Ir}(Cl)(Cl)(PPh_3) \rightarrow Ph_3P{-}\overset{CO}{Ir}(CH_2C_6H_4X)(Cl)(Cl)(PPh_3)} \qquad (41)$$



$$\mathrm{Ph_3P{-}\overset{COCH_2C_6H_4X}{Rh}(Cl)(Cl)(PPh_3) \rightleftharpoons Ph_3P{-}\overset{CO}{Rh}(CH_2C_6H_4X)(Cl)(Cl)(PPh_3)} \qquad (42)$$



$$\mathrm{Ph_3P{-}\overset{COCH_2C_6H_4X}{Rh}(Cl)(Cl)(PPh_3) \rightarrow ClCH_2C_6H_4X + Rh(PPh_3)(CO)(Cl)(PPh_3)} \qquad (43)$$

more electron releasing whereas the rate of reductive elimination (43) decreases as X becomes more electron releasing. When the phenylacetyl group bonded to rhodium is replaced by a benzoyl group, the exact opposite trends are observed [91] as indicated by the appropriate ρ values given in Table 4.

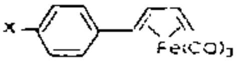
TABLE 4

Summary of correlations involving substituted benzoyl and phenylacetyl complexes

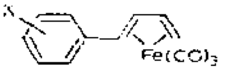
Chemical system	Correlation	Ref.
$(+)\text{-}(\eta^5\text{-}C_5H_5)Mn(NO)(PPh_3)(COC_6H_4X) \rightarrow$ $(-)\text{-}(\eta^5\text{-}C_5H_5)Mn(CO)(PPh_3)(COC_6H_4X)$ $X = H, 4\text{-}CH_3, 4\text{-}OCH_3, 4\text{-}N(CH_3)_2, 4\text{-}C_6H_5,$ $4\text{-}F, 4\text{-}Cl, 4\text{-}CF_3$	$\log k/\sigma$ $\Delta\tau(C_5H_5)/\sigma$ $\rho = -1.8$ (toluene)	113
$IrCl_2(COCH_2C_6H_4X)(PPh_3)_2 \rightarrow IrCl_2\text{-}$ $(CH_2C_6H_4X)(CO)(PPh_3)_2$ $X = 4\text{-}CH_3, 4\text{-}OCH_3, H, 4\text{-}NO_2, 2,3,4,5,6\text{-}F_5$	$\log k/\sigma$ $\rho = -0.30$ (benzene)	114
$RhCl_2(COCH_2C_6H_4X)(PPh_3)_2 \rightleftharpoons RhCl_2\text{-}$ $(CH_2C_6H_4X)(CO)(PPh_3)_2$	$\log k/\sigma$ $\rho = -0.61$ (1,2-dichloroethane)	91
$RhCl_2(CH_2C_6H_4X)(CO)(PPh_3)_2 \rightarrow$ $RhCl(CO)(PPh_3)_2 + ClCH_2C_6H_4X$ $X = 4\text{-}NO_2, 4\text{-}Cl, H, 4\text{-}OCH_3$	$\log k/\sigma$ $\rho = 0.45$ (1,2-dichloroethane)	91
$RhCl_2(COC_6H_4X)(PPh_3)_2 \rightarrow RhCl_2\text{-}$ $(\eta^1\text{-}C_6H_4X)(CO)(PPh_3)_2$	$\log k/\sigma$ $\rho = 0.27$ (1,2-dichloroethane)	91
$RhCl_2(\eta^1\text{-}C_6H_4X)(CO)(PPh_3)_2 \rightarrow$ $RhCl(CO)(PPh_3)_2 + ClC_6H_4X$ $X = 4\text{-}Cl, H, 4\text{-}CH_3, 4\text{-}OCH_3$	$\log k/\sigma$ $\rho = 1.6$ (1,2-dichloroethane)	91

(iii) Olefin and acetylene complexes

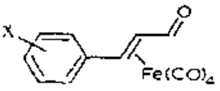
The three ν(CO) frequencies for a series of 4-substituted-1-phenylbutadiene-irontricarbonyl complexes, XI, have each been linearly correlated to σ_p [115]. As expected the ν(CO) frequencies decrease as X becomes more electron releasing and the effect of X is equally transmitted to each CO group. On the other hand there is no apparent correlation between the metal carbonyl ν(CO) frequencies and the σ parameters for XII and XIII [116].



XI



XII



XIII

The rate of dissociation of $Fe(CO)_3(\eta^4\text{-}C_6H_5CH{=}CHCH{=}NC_6H_4X)$ in the presence of PPh_3 is a linear function of σ_p and increases as X becomes a better electron donating group [117]. A similar result has also been reported for $Fe(CO)_3(\eta^4\text{-}XC_6H_4CH{=}CHCHO)$, XII, [118] (X = 4-$N(CH_3)_2$, 4-$OCH_3$, 3-$OCH_3$, 4-$CH_3$ or 4-Cl).

(44)

The pK_a values for $Fe(CO)_4(\eta^2\text{-}XC_6H_4CH{=}CHCO_2H)$ complexes (X = H, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-Cl or 4-Cl) also do not show any correlation with the σ parameters [119] indicating that there is effectively no conjugation between the ring and the ligated exocyclic double bond.

Plots of the ν(CN) frequencies for the $CNBu^t$ ligands in $Ni(CNBu^t)_2(\eta^2\text{-}XC_6H_4CH{=}C(CN)_2)$, $Ni(CNBu^t)_2(\eta^2\text{-}XC_6H_4CH{=}C(CN)H)$, $Ni(CNBu^t)_2(\eta^2\text{-}XC_6H_4CH{=}CHNO_2)$, and $Ni(CNBu^t)_2(\eta^2\text{-}XC_6H_4CH{=}CHCOC_6H_5)$ versus $\Sigma\sigma_p$ all have the same slope [120]. The effect of X is, therefore, equally reflected by ν(CN) for each of these series of complexes.

The rates of addition of HgOAc [121] and CrO_2^{2+} [122] to substituted styrenes have each been correlated to σ^+. The relative rates of the palladium(II)-induced alkylation of substituted styrenes exhibit a good linear correlation with σ [123]. In contrast to the foregoing reactions, the rates of oxidation of substituted cinnamic acids by MnO_4^- at low and high pH are insensitive to the nature of the substituent [124].

The effect of substituents on the cobalt and rhodium catalyzed hydroformylation of a number of substituted styrenes, $XC_6H_4CH{=}CH_2$, has recently been reported [125]. Plots of selectivity and regioselectivity of the products versus σ were examined. The cobalt catalyzed reaction is much more sensitive to the nature and position of X than is the rhodium-catalyzed reaction. A mechanistic explanation for this difference is not yet available.

Some time ago Roy and Orchin [126] observed a "U"-shaped Hammett plot for the equilibrium

$$[(\eta^2\text{-}C_{10}H_{21}CH{=}CH_2)PtCl_3]^- + XC_6H_4CH{=}CH_2 \rightleftharpoons [(\eta^2\text{-}XC_6H_4CH{=}CH_2)PtCl_3]^- + C_{10}H_{21}CH{=}CH_2 \tag{45}$$

Similar Hammett plots were subsequently reported for the equilibrium (46) [127]

$$\textit{trans}\text{-}[PtCl_2(\eta^2\text{-}XC_6H_4CH{=}CH_2)(ONC_5H_4Y)] + C_{10}H_{21}CH{=}CH_2 \rightleftharpoons \textit{trans}\text{-}[PtCl_2(\eta^2\text{-}C_{10}H_{21}CH{=}CH_2)(ONC_5H_4Y)] + XC_6H_4CH{=}CH_2 \tag{46}$$

Although it is possible to discuss the various trends in the equilibrium constants as a function of the substituents X and/or Y, a definitive rationale for these data has yet to be found.

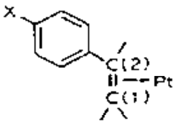
The rates of olefin inversion in the optically active complexes *trans*-N-$[PtCl(\text{L-prol})(\eta^2\text{-4-}XC_6H_4CH{=}CH_2)]$ where prol = prolinate and X = OCH_3, CH_3, H, Cl or NO_2 have been found to increase as X becomes more electron-withdrawing [128].

The pK_a values for *trans*-$[Pt(NH_3)_2(H_2O)(\eta^2\text{-}XC_6H_4CH{=}CH_2)]^{2+}$ (X = 4-Cl, H or 4-OCH_3) increase as X becomes more electron withdrawing [129].

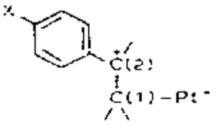
$$\textit{trans}\text{-}[Pt(NH_3)_2(OH_2)(\eta^2\text{-}XC_6H_4CH{=}CH_2)]^{2+} + H_2O \rightleftharpoons \textit{trans}\text{-}[Pt(NH_3)_2(OH)(\eta^2\text{-}XC_6H_4CH{=}CH_2)]^+ + H_3O^+ \tag{47}$$

The chemical shifts of the olefinic protons in a number of $K[PtCl_3(\eta^2\text{-}XC_6H_4CH{=}CH_2)]$ complexes appear to be rather insensitive to the nature of X by virtue of the relatively small slopes obtained when they are plotted versus Hammett's σ parameter [130].

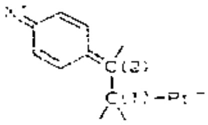
Powell and his co-workers have used ^{1}H and ^{13}C NMR to systematically study substituent effects associated with styrenes coordinated to Pt(II) [131,132] and Pd(II) [133,134]. For the complexes, *trans*-$[PtCl_2(NC_5H_4\text{-4-}CH_3)(\eta^2\text{-}XC_6H_4CH{=}CH_2)]$, *trans*-$[PtCl(NH_3)_2(\eta^2\text{-}XC_6H_4CH{=}CH_2)]^+$, and $[PtCl_3(\eta^2\text{-}XC_6H_4CH{=}CH_2)]^-$ [132] the quantities $^1J[Pt{-}C(1)]$, $^1J[Pt{-}C(2)]$, $\delta_C[C(1)]$, $\delta_C[C(2)]$, and $\Delta^1J[Pt{-}C]/J_{\text{mean}}$ (X = NO_2) were plotted versus σ^+ to yield straight lines which can be interpreted in terms of the canonical structures XIV, XV and XVI. Electron donating substituents increase the contribution of XV and/or XVI and the distance between C(1) and Pt should



XIV



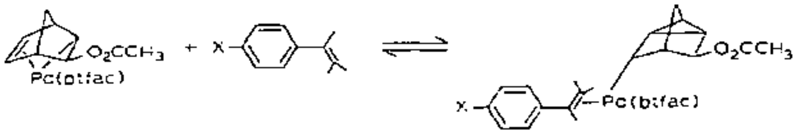
XV



XVI

decrease as X becomes more electron releasing. This latter suggestion has been confirmed by X-ray structural analyses for *trans*-[$PtCl_2(NC_5H_4$-4-CH_3)(η^2-$XC_6H_4CH{=}CH_2$)] (X = 4-$N(CH_3)_2$, H) and *trans*-$PtCl_2(NC_5H_4$-4-Cl)(η^2-4-$NO_2C_6H_4CH{=}CH_2$)] [135]. Reasonable linear plots were obtained when the Pt—C(1) or Pt—C(2) distances were plotted versus σ^+ for the styrene substituents and the Pt—C(1) distance lengthened with increasing value of σ^+. The ν(Pt—Cl) frequency for Cl *trans* to $XC_6H_4CH{=}CH_2$ as well as the "ν(Pt—C_2(ring))" mode for [$PtCl_3(\eta^2$-$XC_6H_4CH{=}CH_2)]^-$ are also linearly correlated to σ^+ [132].

The equilibrium constants for eqn. (48) are linearly correlated to σ^+ ($\rho = 0.54$) but not to Hammett's σ parameter which can be interpreted in terms of the relative contributions of XIV—XVI [133,134].



(48)

The rate of the electrophilic reaction

$$(\eta^1\text{-}XC_6H_4C_2)_2Hg + HCl \rightarrow (\eta^1\text{-}XC_6H_4C_2)HgCl + XC_6H_4C_2H \qquad (49)$$

has been correlated to $(\sigma + \sigma^+)/2$ [136] with $\rho = -1.0$ indicating that it is less sensitive to the nature of X than the analogous reaction with $(\eta^1\text{-}XC_6H_4)_2Hg$ derivatives [95].

Equilibrium constants and kinetic data for the forward and reverse reactions of

$$(Ph_3P)_2Pt(\eta^2\text{-}XC_6H_4C_2H) + YC_6H_4C_2H \rightleftharpoons (Ph_3P)_2Pt(\eta^2\text{-}YC_6H_4C_2H) + \\ + XC_6H_4C_2H \qquad (50)$$

are sensitive to the nature of X [137,138]. The equilibrium favours the reactants as the substituents become more electron attracting and the first order rate constants decrease as the substituents become more electron withdrawing. A good Hammett correlation has also been reported between log (K/K_0) and σ [139]. The rate of the ligand exchange

$$(Ph_3P)_2Pt(\eta^2\text{-}XC_6H_4C_2H) + 4\text{-}NO_2C_6H_4C_2H \rightleftharpoons (Ph_3P)_2Pt(\eta^2\text{-}4\text{-}NO_2C_6H_4C_2H) \\ + XC_6H_4C_2H \qquad (51)$$

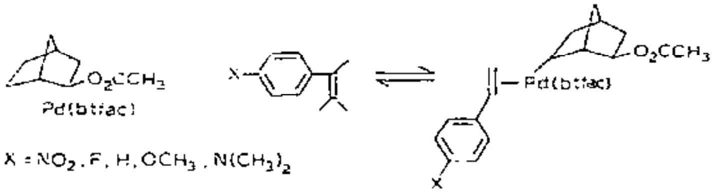
has also been correlated to Hammett's σ^0 parameter giving a reaction constant, $\rho = -1.20$ which has been interpreted in terms of the presence of a radical stabilized acetylenic ligand at the metal center in the transition state [140]. Moreover, it has since been shown that both associative and dissociative pathways are involved in the intimate mechanism of these exchange reactions [141]. Correlations involving the foregoing systems are summarized in Table 5.

TABLE 5

Summary of correlations for olefin and acetylene complexes

Chemical system	Correlation	Ref.
$(\eta^4\text{-}4\text{-}XC_6H_4CH{=}CHCH{=}CH_2)Fe(CO)_3$ X = NH_2, OCH_3, H, $NHCOCH_3$, Br, $COCH_3$, CN	$\nu(CO)\ (cm^{-1})/\sigma_p$	115
$(\eta^4\text{-}C_6H_5CH{=}CHCH{=}NC_6H_4X)Fe(CO)_3 \rightleftharpoons (\eta^2\text{-}C_6H_5CH{=}CHCH{=}NC_6H_4X)Fe(CO)_3$ X = 4-NH_2, 4-OCH_3, H, 4-CH_3, 4-Br	$\log k/\sigma_p$	117
$Ni(CNBu^t)_2(\eta^2\text{-}XC_6H_4CH{=}C(CN)_2)$ X = 3-OCH_3, 4-F, 2,5-$(OCH_3)_2$, 4-Cl, 4-CN, 4-NO_2, 4-$N(CH_3)_2$	$\nu(CN)^a\ (cm^{-1})/\Sigma\sigma_p$	120
$Ni(CNBu^t)_2(\eta^2\text{-}XC_6H_4CH{=}C(CN)H)$ X = 4-$N(CH_3)_2$, 4-OCH_3, 3,4-$(CHO)_2$, H, 4-Cl	$\nu(CN)^a\ (cm^{-1})/\Sigma\sigma_p$	120
$Ni(CNBu^t)_2(\eta^2\text{-}XC_6H_4CH{=}C(NO_2)H)$ X = 3,4-$(OCH_3)_2$, H, 3-F-4-OCH_3, 2-OCH_3-5Br, 4-Cl, 2-Br, 3-CN, 3,4-Cl_2	$\nu(CN)^a\ (cm^{-1})/\Sigma\sigma_p$	120
$Ni(CNBu^t)_2(\eta^2\text{-}XC_6H_4CH{=}C(COC_6H_5)H)$ X = 4-OCH_3, H, 4-Cl, 4-NO_2	$\nu(CN)^a\ (cm^{-1})/\Sigma\sigma_p$	120
$XC_6H_4CH{=}CH_2/CrO_2^{2+}$ X = H, 4-CH_3, 4-C_6H_5, 4-Cl, 4-Br, 3-Cl, 4-NO_2	$\log k/\sigma^+$ $\rho = -1.99$	122
$XC_6H_4CH{=}CH_2/HgOAc$ X = H, 3-Cl, 4-Cl, 3-Br, 4-Br, 3-CH_3, 4-CH_3, 3-NO_2, 4-OCH_3	$\log k/\sigma^+, \sigma$	121
$XC_6H_4CH{=}CH_2 \xrightarrow[Pd(acac)_2]{CH_3Li} XC_6H_4CH{=}CH(CH_3)$ X = 3-Cl, 4-Cl, H, 4-CH_3, 4-OCH_3	$\log k/\sigma$ $\rho = 2.7$ (THF)	121
$XC_6H_4CH{=}CH_2/Co_2(CO)_8/CO, H_2$ $XC_6H_4CH{=}CH_2/Rh\text{-}Al_2O_3, PPh_3/CO, H_2$ X = 2-CH_3, 3-CH_3, 4-CH_3, 2,6-$(CH_3)_2$, 2-OCH_3, 3-OCH_3, 4-OCH_3, 2-Cl, 3-Cl, 4-Cl, 2,6-Cl_2, 3,4-Cl_2	S, RS/σ^c S, RS/σ^c	125
$[(\eta^2\text{-}C_{10}H_{21}CH{=}CH_2)PtCl_3]^- + XC_6H_4CH{=}CH_2 \rightarrow [(\eta^2\text{-}XC_6H_4CH{=}CH_2)PtCl_3]^- + C_{10}H_{21}CH{=}CH_2$ X = 4-OCH_3, 4-CH_3, H, 3-OCH_3, 3-Cl, 4-NO_2	$\log K/\sigma$	126
trans-$[PtCl_2(\eta^2\text{-}XC_6H_4CH{=}CH_2)$-	$\log K/\sigma$	127

TABLE 5 (Continued)

Chemical system	Correlation	Ref.
(ONpyY)] + $C_{10}H_{21}CH{=}CH_2 \rightleftharpoons$ *trans*-[$PtCl_2(\eta^2\text{-}C_{10}H_{21}CH{=}CH_2)$-(ONpyY)] + $XC_6H_4CH{=}CH_2$ X = 3-OCH_3, 4-OCH_3, H, 3-CH_3, 4-CH_3, 3-Cl, 4-Cl, 3-NO_2, 4-NO_2 Y = 4-OCH_3, 4-CH_3, H, 4-Cl, 4-CO_2CH_3, 4-NO_2		
K[$PtCl_3(\eta^2\text{-}XC_6H_4CH{=}CH_2)$] X = 4-$OCH_3$, 4-$CH_3$, H, 4-Cl, 3-$NO_2$, 4-$NO_2$	$\delta(^1H)$ (ppm)/σ	130
trans-[$PtCl_2(\text{py-4-}CH_3)(\eta^2\text{-}XC_6H_4CH{=}CH_2)$]	$\delta(^{13}C)$ (ppm)/σ^+, $J(Pt{-}^{13}C)$ (Hz)/σ^+	131, 132
trans-[$PtCl(NH_3)_2(\eta^2\text{-}XC_6H_4CH{=}CH_2)$]$^+$	$\delta(^{13}C)$ (ppm)/σ^+, $J(Pt{-}^{13}C)$ (Hz)/σ^+	131, 132
[$PtCl_3(\eta^2\text{-}XC_6H_4CH{=}CH_2)$]$^-$ X = 4-$N(CH_3)_2$, 4-OC_2H_5, 4-OC_6H_5, 4-CH_3, H, 4-Cl, 4-$COCH_3$, 4-NO_2	$\delta(^{13}C)$ (ppm)/σ^+, $J(Pt{-}^{13}C)$ (Hz)/σ^+ $\nu(Pt{-}Cl)$ (cm^{-1})/σ^+ "$\nu(Pt{-}C_2)$ ring" (cm^{-1})/σ^+	131, 132
	log K/σ^+	133, 134
trans-[$PtCl_2(\text{py-4}CH_3)(\eta^2\text{-}XC_6H_4CH{=}CH_2)$]	Pt—C(1) (Å)/σ^+	135
trans-[$PtCl_2(\text{py-4}Cl)(\eta^2\text{-4}NO_2C_6H_4CH{=}CH_2)$] X = $N(CH_3)_2H$	Pt—C(2) (Å)/σ^+	
$(\eta^1\text{-}XC_6H_4C_2)_2Hg + HCl \rightarrow (\eta^1\text{-}XC_6H_4C_2)HgCl + XC_6H_4C_2H$ X = H, 4-F, 4-Cl, 3-Cl, 3-CH_3, 2,4-$(CH_3)_2$	$\log k/\frac{(\sigma+\sigma^+)}{2}$ $\rho = -1.0$ (DMSO-dioxane)	136
$(Ph_3P)_2Pt(\eta^2\text{-}XC_6H_4C_2H) + YC_6H_4C_2H \rightleftharpoons (Ph_3P)_2Pt(\eta^2\text{-}YC_6H_4C_2H) + XC_6H_4C_2H$ X, Y = one of 4-NO_2, 4-Br, 4-Cl, H, 4-OCH_3, 3-NO_2, 2-Cl, 2-F, 4-F, 2-OCH_3, 3-OCH_3	$\log(K/K_0)/\sigma$	139
$(Ph_3P)_2Pt(\eta^2\text{-}XC_6H_4C_2H)$ + 4-$NO_2C_6H_4C_2H \rightleftharpoons (Ph_3P)_2Pt$-(4-$NO_2C_6H_4C_2H$) + $XC_6H_4C_2H$ X = 3-OCH_3, 3-NO_2, 4-OCH_3, 4-CH_3, 3-CH_3, 4-F, 4-Cl, 3-NO_2, 4-NO_2	$\log k/\sigma^0$	140

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[a] ν(CN) for isocyanide ligand. [b] Products of reaction are $XC_6H_4CH_2CHO$ and $XC_6H_4CH_2CH_3$. [c] S = selectivity, RS = regioselectivity.

(iv) Isocyanide complexes

The half wave potentials for the sequential one-electron oxidation of a number of *para*- and *meta*-substituted hexakis(arylisocyanide)chromium(0) complexes, $[Cr(CNC_6H_4X)_6]$

$$[Cr(CNC_6H_4X)_6]^- \rightleftharpoons [Cr(CNC_6H_4X)_6]^0 + e^- \qquad (52)$$

$$[Cr(CNC_6H_4X)_6]^0 \rightleftharpoons [Cr(CNC_6H_4X)_6]^+ + e^- \qquad (53)$$

$$[Cr(CNC_6H_4X)_6]^+ \rightleftharpoons [Cr(CNC_6H_4X)_6]^{2+} + e^- \qquad (54)$$

gave excellent correlations with Hammett's σ parameters showing that these oxidation processes are sensitive to both inductive and resonance contributions of X [142]. Similar correlations are also observed for manganese complexes

$$[Mn(CNC_6H_4X)_6]^+ \rightleftharpoons [Mn(CNC_6H_4X)_6]^{2+} + e^- \qquad (55)$$

Reaction constants for these oxidation processes have been calculated using eqn. (56) (see Table 6).

$$\Delta E_{1/2} = 6\,\rho\sigma \qquad (56)$$

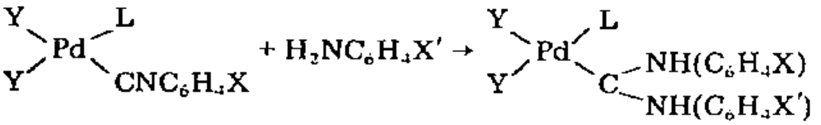
For the parent complexes, $[Cr(CNC_6H_4X)_6]$ and $[Mn(CNC_6H_4X)_6]^+$ neither $\nu(CN)$ nor $\Delta\nu(CN)$ $(\nu(CN)_{\text{free ligand}} - \nu(CN)_{\text{coordinated ligand}})$ correlated with the σ parameters. Similar results have been obtained for the one-electron oxidation shown in eqn. (57) where M = Mo or W [144].

$$[M(diphos)_2(CNC_6H_4X)_2] \rightleftharpoons [M(diphos)_2(CNC_6H_4X)_2]^+ + e^- \qquad (57)$$

Recently an explanation has been put forward to account for the apparent insensitivity of the $\nu(CN)$ frequency to changes in substituents for coordinated NCC_6H_4X ligands [145]. However the $\nu(CN)$ frequency of a coordinated isocyanide can be correlated to a substituent effect originating on a co-ligand as observed in $Ni(CNBu^t)_2$(olefin) complexes [120]. Also it is interesting to note that for analogous series of isocyanide complexes, *trans*-$[Pt(CH_3)(PMe_2Ph)_2(CNC_6H_4X)]^+$ [146] and nitrile complexes, *trans* $[Pt(CH_3)(PMe_2Ph)_2(NCC_6H_4X)]^+$ [147], only the $\nu(CN)$ frequencies for the nitrile derivatives correlate with the anticipated electronic effect of X.

The ^{13}C NMR chemical shifts for the isocyanide carbon atom or the aromatic carbon atom attached to the nitrogen atom of the arylisocyanide in the complexes, *cis*-$[PtCl_2(CNC_6H_4X)(PEt_3)]$ and *trans*-$[PtY(CNC_6H_4X)(PEt_3)_2]^+$ (Y = Cl or Br) each gave a good linear correlation with the σ^+ parameter indicating that the electronic effect of X can be transmitted to the isocyanide carbon atom [148].

This particular substituent effect also manifests itself in the kinetic data for



$$Y_2Pd(L)(CNC_6H_4X) + H_2NC_6H_4X' \rightarrow Y_2Pd(L)\{C(NH(C_6H_4X))(NH(C_6H_4X'))\} \qquad (58)$$

where L = PPh_3 or $AsPh_3$ and Y = Cl or Br [149]. The second order rate constants vary linearly with the σ parameter for X and X′ and increase as both X and X′ become more electron withdrawing.

The $\sigma \rightarrow \sigma^*$ transition which occurs in the near UV and is associated with the metal—metal bond in $Co_2(2,6\text{-}Me_2\text{-}4\text{-}XC_6H_2NC)_8$ complexes shows a linear correlation with Hammett's σ parameter for X [150]. As the energy of this transition shifts to lower energy, X becomes more electron releasing.

Correlations involving these substituted isocyanide complexes are summarized in Table 6.

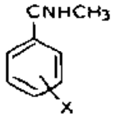
(v) Carbene complexes

Substituent effects in metal complexes containing the carbene moieties XVII—XXI have been investigated by several workers [151—159].

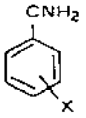
TABLE 6

Summary of correlations for isocyanide complexes

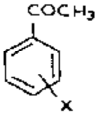
Chemical system	Correlation	Ref.
$[Cr(CNC_6H_4X)_6]^- \rightleftharpoons [Cr(CNC_6H_4X)_6]^0 + e^-$	$E_{1/2}$ (V)/σ $\rho = 0.070$ (CH_3CN)	142
$[Cr(CNC_6H_4X)_6]^0 \rightleftharpoons [Cr(CNC_6H_4X)_6]^+ + e^-$	$E_{1/2}$ (V)/σ $\rho = 0.085$ (CH_3CN)	142
$[Cr(CNC_6H_4X)_6]^+ \rightleftharpoons [Cr(CNC_6H_4X)_6]^{2+} + e^-$	$E_{1/2}$ (V)/σ $\rho = 0.080$ (CH_3CN)	142
X = 4-$N(CH_3)_2$, 4-OCH_3, 4-CH_3, 3-CH_3, H, 4-F, 3-OCH_3, 4-Cl, 4-Br, 3-Cl, 3-CF_3		
$[Mn(CNC_6H_4X)_6]^+ \rightleftharpoons [Mn(CNC_6H_4X)_6]^{2+} + e^-$ X = 4-OCH_3, 4-CH_3, 3-CH_3, H, 4-F, 4-Cl, 4-Br, 3-CF_3, 4-CN, 4-NO_2	$E_{1/2}$ (V)/σ $\rho = 0.073$ (CH_2Cl_2)	143
$[M(diphos)_2(CNC_6H_4X)_2] \rightleftharpoons [M(diphos)_2(CNC_6H_4X)_2]^+ + e^-$ X = 4-Cl, H, 4-CH_3, 4-OCH_3	$E_{1/2}$ (V)/σ	144
cis-$[PtCl_2(CNC_6H_4X)(PEt_3)]$ *trans*-$[PtY(CNC_6H_4X)(PEt_3)_2]$ Y = Cl, Br; X = H, 4-CH_3, 4-OCH_3, 4-Cl, 4-NO_2	$\delta(^{13}C)$ (ppm)/σ^+	148
cis-$[PdY_2L(CNC_6H_4X)] + H_2NC_6H_4X' \rightarrow [PdY_2LC(NHC_6H_4X)(NHC_6H_4X')]$ X = 4-CH_3, 4-CH_3, H, 4-NO_2 X′ = 4-OCH_3, 4-CH_3, H, 4-Cl, 4-NO_2 Y = Cl, Br	log k/σ	149
$Co_2(2,6\text{-}Me_2\text{-}4\text{-}XC_6H_2NC)_8$ X = H, CH_3, Br	$\bar{\nu}(\sigma \rightarrow \sigma^*)$ (cm^{-1})/σ_p	150



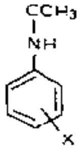
XVII



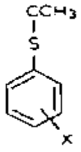
XVIII



XIX



XX



XXI

The ^{13}C chemical shifts of the carbene carbon atom in *trans*-[Pt(Me)-$(AsMe_3)_2C(NHMe)(C_6H_4X)]PF_6$ complexes have been correlated to the σ^+ parameters of the substituents indicating that there are both σ and π interactions between the phenyl ring and the carbene carbon atom [151].

The ionization potentials for $Cr(CO)_5C(NH_2)(C_6H_4X)$ derivatives increase linearly with increasing value of Hammett's σ constant [152]. A plot of the force constant, k_{CO} for the CO group *trans* to the $C(NH_2)(C_6H_4X)$ moiety versus σ is linear; k_{CO} decreases as X becomes more electron releasing, which is consistent with an increase in electron density at the metal center [153]. A similar correlation involving k_{CO} as well as the ionization potential has been noted for $Cr(CO)_5C(OCH_3)(C_6H_4X)$ complexes when $\sigma < 0$ for X but not when $\sigma > 0$ for X [154,155]. The exact reason for this difference is not readily apparent.

Variations in the $\nu(CO)$ frequencies, ^1H NMR chemical shifts for the NH and CH_3 protons, dipole moments, and ionization potentials for $Cr(CO)_5$

TABLE 7

Summary of correlations involving carbene complexes

Chemical system	Correlation	Ref.
trans-$[Pt(Me)(AsMe_3)_2C(NHMe)(C_6H_4X)]PF_6$ X = 4-Br, 4-Cl, H, 4-CH_3, 4-OCH_3	$\delta_{carbene}(^{13}C)$ (ppm)/σ^+	151
$M(CO)_5C(CH_3)(SC_6H_4X)$ M = Cr or W X = 4-OH, 4-OCH_3, 4-CH_3, 4-F, H, 4-Br	$\delta_{carbene}(^{13}C)$ (ppm)/σ^n, σ^+	158
$Cr(CO)_5C(NH_2)(C_6H_4X)$ X = 4-$N(CH_3)_2$, 4-OCH_3, 4-CH_3, H, 4-Cl, 4-Br, 3-OCH_3, 3-Cl	I.P. (eV)/σ k_{CO} (mdyne cm^{-1})/σ	152 153
$Cr(CO)_5C(OCH_3)(C_6H_4X)$ X = 4-$N(CH_3)_2$, 4-OCH_3, 4-CH_3, 4-F, 4-Cl, 4-Br, 4-CF_3, 3-$N(CH_3)_2$, 3-OCH_3, 3-Cl, 3-CF_3, 2-OCH_3, 2-CF_3, 2,4,6-$(CH_3)_3$, 2,6-$(OCH_3)_2$	I.P. (eV)/σ k_{CO} (mdyne cm^{-1})/σ	154, 155
$(CO)_5WC(OCH_3)(C_6H_4X) + PBu^n_3 \rightleftharpoons (CO)_5WC(OCH_3)(C_6H_4X)(PBu^n_3)$	log K/σ $\Delta H/\sigma$ log K/k_{CO}(mdyne cm^{-1})	159

$C(CH_3)(NHC_6H_4X)$ ($X = 4\text{-}NH_2$, $4\text{-}OCH_3$, $4\text{-}CH_3$, H, 4-Cl or $4\text{-}CF_3$) have been discussed in terms of the σ_p parameters for the various types of X groups [156]. Anomalies were also noted for this series of complexes when $\sigma > 0$ for a given X group as previously noted for the methoxy phenyl carbene complexes.

For complexes of the type, $M(CO)_5C(CH_3)(SC_6H_4X)$(M = Cr or W) [157] both ν(CO) (for the CO group *trans* to the carbene ligand) and the ^{13}C chemical shift for the carbene atom are insensitive to the nature of X. However, a detailed correlation analysis of the ^{13}C NMR parameters for the carbene carbon and the ring carbon atoms with σ^n and σ^* suggests that there are both σ and π interactions between the ring and the carbene carbon [158].

Recently, equilibrium data for

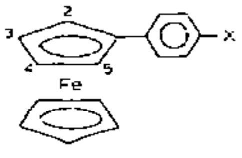
$$(CO)_5WC(OCH_3)(C_6H_4X) + PBu^n_3 \rightleftharpoons (CO)_5WC(OCH_3)(C_6H_4X)(PBu^n_3) \qquad (59)$$

in toluene have been reported. Both log K and ΔH are linearly correlated to σ and as expected ΔH decreases and log K increases as X becomes more electron-withdrawing which is consistent with the electrophilic nature of the carbene carbon atom [159]. In addition a plot of log K versus k_{CO} was linear and the equilibrium shifted to the right with increasing value of the force constant, k_{CO}.

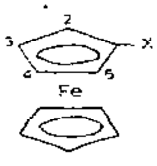
The foregoing correlations are summarized in Table 7.

(vi) Other complexes

For XXII, when the average 2,5 and 3,5 proton chemical shifts are plotted versus Hammett's σ_p parameter a good linear correlation (neglecting X = Cl) is obtained with a slope of −0.21 [160].



XXII



XXIII

The phenyl ring apparently exerts an insulating effect since the slope of the corresponding plot for XXIII is −0.90 ($X = CH_3$, C_2H_5, $i\text{-}C_3H_7$, $t\text{-}C_4H_9$, H, $COCH_3$, COC_6H_5, CO_2CH_3). A plot of the chemical shifts for the C_5H_5 protons for XXII versus σ_p is also linear with a slope equal to −0.029. Consequently, a ρ ratio of 0.029/0.21 = 0.14 can be calculated [147] which implies that 14% of the electronic effect of X is transmitted to the cyclopentadienyl ring through the ferrocene moiety. The formal one-electron oxidation potentials for XXII also show a linear correlation with σ and increase as X becomes more electron releasing which is consistent with the qualitative observation that electron releasing substituents on the C_5H_5 ring facilitate oxidation of ferrocene derivatives [161].

TABLE 8

Summary of correlations involving complexes containing a remote substituted phenyl ring and a metal—carbon bond

Chemical system	Correlation	Ref.
$[\eta^5\text{-}C_5H_4(C_6H_4X)]Fe(\eta^5\text{-}C_5H_5)$ X = $4\text{-}OCH_3$, H, $4\text{-}COCH_3$, 4-Cl, $4\text{-}NO_2$	$\delta_{C_5H_4}$ (^{1}H) (ppm)/σ	160
$[\eta^5\text{-}C_5H_4(C_6H_4X)]Fe(\eta^5\text{-}C_5H_5)/[\eta^5\text{-}C_5H_4\text{-}(C_6H_4X)Fe(\eta^5\text{-}C_5H_5)^+$ X = $4\text{-}OCH_3$, H, 4-Cl, 4-Br, $4\text{-}COCH_3$, $4\text{-}NO_2$	$\log(K/K_0)/\sigma$ $\rho = -2.41$ (acetic acid/$HClO_4$)	161
X = $2\text{-}NO_2$, 2-F, 2-Cl, 2-Br, 2-I, $2\text{-}CH_3$, $2\text{-}OCH_3$, $2\text{-}OC_2H_5$, $4\text{-}NO_2$, 4-CN, 3-CN, $3\text{-}CO_2C_2H_5$, $4\text{-}COCH_3$, $4\text{-}CO_2H$, $3\text{-}CF_3$, $3\text{-}CO_2C_2H_5$, 3-Br, $3\text{-}CO_2H$, 4-Br, 4-Cl, $4\text{-}C_6H_5$, H, $3\text{-}NH_2$, $4\text{-}CH_3$, $4\text{-}OCH_3$, 4-OH, $4\text{-}NH_2$	$E_{1/4}$ (V)/σ $\Delta E_{1/4} = 0.128\sigma + 0.024$ V[a] $\Delta E_{1/4} = 0.126\sigma_0^* + 0.031$ V[b]	162 163
$[\eta^4\text{-}C_4H_3(C_6H_4X)]Fe(CO)_3$ X = 4-F, 4-Cl, 4-Br, H	$\delta_{C(5)}$ (^{13}C) (ppm)[c]/σ, σ_p^0	165
$(\eta^3\text{-}2\text{-}(C_6H_4X)\text{-}C_3H_4)Pd(acac)$ $(\eta^3\text{-}2\text{-}(C_6H_4X)\text{-}C_3H_4)Pd(\eta^5\text{-}C_5H_5)$ $(\eta^3\text{-}1\text{-}(C_6H_4X)\text{-}C_3H_4)Pd(acac)$ $(\eta^3\text{-}1\text{-}(C_6H_4X)\text{-}C_3H_4)Pd(\eta^5\text{-}C_5H_5)$ X = 4-Br, 4-Cl, H, $4\text{-}CH_3$, $4\text{-}OCH_3$	$\delta_{C_6H_4X}$ (^{1}H) (Hz)/σ_p^+	166
$2(\eta^1\text{-}XC_6H_4CHCO_2Et)HgBr \rightarrow (\eta^1\text{-}XC_6H_4CHCO_2Et)_2Hg + HgBr_2$ X = $4\text{-}NO_2$, 4-I, 4-Br, 3-Br, 2-Br, 4-Cl, 4-F, H, $4\text{-}CH_3$, $3\text{-}CH_3$, $2\text{-}CH_3$, $4\text{-}C_2H_5$, $4\text{-}i\text{-}C_3H_7$, $4\text{-}t\text{-}C_4H_9$	$\log(k/k_0)/\sigma$ $\rho = 2.85$	167
$(\eta^5\text{-}C_5H_3\text{-}1,2\text{-}(C_6H_4X)_2)_2Fe$	$\Delta E_{1/4}$ (V)/σ	164
$(\eta^5\text{-}C_5H_4\text{-}C_6H_4N_2C_6H_4X)Fe(\eta^5\text{-}C_5H_5)$	$E_{1/2}$ (V)/σ	163

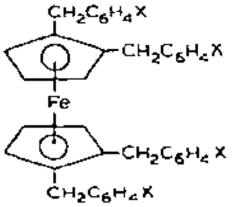
[a] $\Delta E_{1/4} = E_{1/4}$ (V) for substituted derivative $- E_{1/4}$ (V) for unsubstituted derivative.
[b] σ_0^* = Taft's *ortho*-substituent constant [168]. [c] C(5) is carbon atom of cyclobutadiene ring bonded to the phenyl ring.

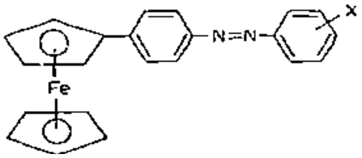
Chronopotentiometric quarter wave potentials, $E_{1/4}$, for the oxidation of XXII also show a linear correlation with σ according to eqn. (60) [162].

$$E_{1/4} = 0.132\,\sigma + 0.361 \tag{60}$$

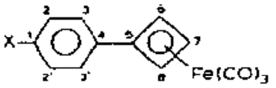
The values of several substituent constants have also been determined from chronopotentiometric data for XXII [163] (See Table 8).

For the complexes, XXIV, $\Delta E_{1/4}$ shows a linear correlation with σ for various substituents, X [164].


XXIV

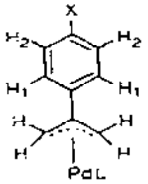

XXV

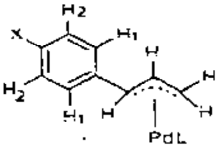
The transmission of electronic effects through a substituted phenylazo group as in XXV has been studied and as expected a small variation (ρ = 0.016) in $E_{1/2}$ with respect to σ was observed [163].


XVI

The ^{13}C chemical shifts for C(5) of XVI show a linear correlation with Hammett's σ and Taft's σ_p^0 parameters suggesting that the $(\eta^4\text{-}C_4H_3)$ $Fe(CO)_3$ group donates electrons via its π-electron system and accepts electrons via its carbon σ-skeletal framework [165]. In contrast to XI (see page 136) the ν(CO) frequencies of XXVI are insensitive to the nature of X.

The chemical shift differences, $\Delta\nu$ (Hz), between the *para*-phenylene ring protons H_1 and H_2 show linear correlations with the σ_p^+ parameter for XXVII—XXX [166]. Also, from the intercepts at $\Delta\nu = 0$ for these plots, the substituent constants of the 1- and 2-positions of the allylic group were estimated [166].


XXVII L = acac
XXVIII L = η^5–C_5H_5


XXIX L = acac
XXX L = η^5–C_5H_5

Electron accepting substituents have been shown to increase the rate of the symmetrication reaction

$$2(\eta^1\text{-}XC_6H_4CHCO_2Et)HgBr \rightarrow (\eta^1\text{-}XC_6H_4CHCO_2Et)_2Hg + HgBr_2 \qquad (61)$$

and $\rho = 2.85$ was obtained from the Hammett plot of log k/k_0 versus σ [167] which is in agreement with an S_E1 type of mechanism involving a four center transition state.

The foregoing correlations are summarized in Table 8.

D. COMPLEXES CONTAINING A REMOTE SUBSTITUTED PHENYL RING AND NO METAL—CARBON BOND

(i) Monodentate ligands

Anilines

The rate of substitution of a coordinated aniline by thiourea

$$[Co(DH)_2(tu)(H_2NC_6H_4X)]^+ + tu \rightarrow [Co(DH)_2(tu)_2]^+ + H_2NC_6H_4X \qquad (62)$$

decreases as the basicity of the free aniline increases [169]. A good Hammett plot of log k versus σ was obtained for all the substituents studied with the exception of the NO_2 group (see Table 9). The positive reaction constant suggests that there is some transfer of electron density from cobalt to the aniline ligand.

Several correlations involving substituted anilines as nucleophiles have been reported [170—172]. A good correlation between log K and σ has been reported for eqn. (63) where as expected electron donating substituents increase the value of the equilibrium constant [170].

$$Co(tu)_2Cl_2 + H_2NC_6H_4X \rightleftharpoons Co(tu)(H_2NC_6H_4X)Cl_2 + tu \qquad (63)$$

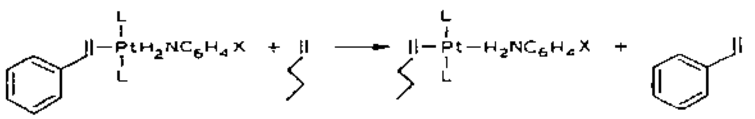
This result is in contrast to the poor correlation reported by Rakshys [171] between σ and the equilibrium constants for adduct formation involving a substituted aniline and $[Ni(acac)_2]$

$$[Ni(acac)_2]_3 + 6\ H_2NC_6H_4X \rightleftharpoons 3(XC_6H_4NH_2)_2Ni(acac)_2 \qquad (64)$$

Substituted anilines as second coordination sphere ligands interacting with $Co(HBpz_3)_2$ complexes have also been investigated in CCl_4 [172]. The ^1H NMR contact shifts for the hydrogens *ortho* to the NH_2 group show a reasonable correlation with σ and increase in frequency as the substituent becomes more electron withdrawing which is consistent with the expected enhancement in axial binding to the cobalt complex since the inner sphere ligands are considered to be negatively charged.

The substituent effect associated with the addition of a substituted aniline across the C≡N bond of a coordinated isocyanide has already been mentioned [149] (see page 141).

The rate of styrene substitution by 1-pentene according to



(65)

decreases as X becomes more electron releasing and the appropriate Hammett plot of log k versus σ yielded a ρ value of 0.86 [173]. This result is interesting in that it is contrary to what would be predicted in terms of the *trans* effect theory for square planar complexes [174].

TABLE 9

Summary of correlations involving complexes with a remote substituted phenyl ring and no metal—carbon bond

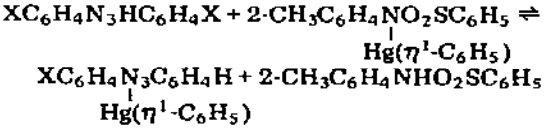
Chemical system	Correlation	Ref.
Substituted aniline complexes		
$Co(DH)_2(tu)(H_2NC_6H_4X)]^+ + tu \rightarrow [Co(DH)_2(tu)_2]^+ + H_2NC_6H_4X$ X = 4-OCH_3, 4-CH_3, 3-CH_3, H, 4-Br, 4-I, 4-NO_2	$\log(k/k_0)/\sigma$ $\rho = 0.65$	169
$Co(tu)_2Cl_2 + H_2NC_6H_4X \rightleftharpoons Cotu(H_2NC_6H_4X)Cl_2 + tu$ X = 4-CH_3, 4-OCH_3, H, 4-Cl, 4-Br, 4-NO_2	$\log K/\sigma$	170
$(XC_6H_4NH_2)Co(HBpz_3)_2$ X = 4-CF_3, H, 4-OCH_3, 4-$N(CH_3)_2$	ν (Hz) (^{1}H NMR)$^a/\sigma$	172
trans-$[Pt(PPh_3)_2(C_6H_5CH{=}CH_2)(H_2NC_6H_4X)] + C_5H_{10} \rightarrow$ *trans*-$[Pt(PPh_3)_2(C_5H_{10})(H_2NC_6H_4X)] + C_6H_5CH{=}CH_2$	$\log k/\sigma$ $\rho = 0.86$ ($CHCl_3$)	173
Substituted aryl diazenido and triazenide complexes		
$[Pt(PPh_3)_3(N_2C_6H_4X)]^+$, $[Pt(PPh_3)_3(N_2HC_6H_4X)]^{2+}$ X = 4-OCH_3, 4-CH_3, 4-F, H, 4-NO_2, 4-$N(CH_3)_2$, 4-$N(C_2H_5)_2$	$n \rightarrow \pi^*$ (cm^{-1})$/\sigma$	177
$RuCl_3(N_2C_6H_4X)(PPh_3)_2$ X = 4-NO_2, 4-OCH_3, 4-CH_3	B.E. (eV) $3p_{3/2}/\sigma$ B.E. (eV) $3d_{5/2}/\sigma$	178
$Mo(N_2C_6H_4X)(S_2CNMe_2)_3$ X = 4-OCH_3, 4-CH_3, H, 4-Cl, 3-NO_2, 4-NO_2	$^b 1/\tau/\sigma$	184
$Mo(N_2C_6H_4X)(S_2CNMe_2)_3/Mo(N_2C_6H_4X)(S_2NMe_2)_3^+$ X = 4-NO_2, 3-NO_2, 3-Cl, 4-Cl, 3-OCH_3, H, 4-F, 3-CH_3, 4-CH_3, 4-OCH_3	$E_{1/2}$ (V)$/\sigma$ $\rho = 5.70$ (DMF)	185
$[IrCl(CO)(PPh_3)_2(N_2C_6H_4X)]BF_4$ X = 4-NO_2, 3-NO_2, 2-NO_2, 2-CN, 4-CN, 4-OCH_3	$n \rightarrow \pi^*$ (cm^{-1})$/\sigma$	181
$IrCl_2(CO)(PPh_3)_2(N_2C_6H_4X)$ X = 4-NO_2, 3-NO_2, 2-NO_2, 4-CN, 2-CN, 4-OCH_3, 3-$COCH_3$, 2-$COCH_3$	$n \rightarrow \pi^*$ (cm^{-1})$/\sigma$	181
 $XC_6H_4N_3HC_6H_4X + 2\text{-}CH_3C_6H_4\underset{\mid \atop Hg(\eta^1\text{-}C_6H_5)}{N}O_2SC_6H_5 \rightleftharpoons XC_6H_4\underset{\mid \atop Hg(\eta^1\text{-}C_6H_5)}{N_3}C_6H_4H + 2\text{-}CH_3C_6H_4NHO_2SC_6H_5$ X = H, 4-CH_3, 4-OCH_3, 4-F, 3-F, 2-CH_3, 2-OCH_3, 2-F, 2-Cl, 2-Br, 2-I	$\log K = 1.6\sigma_0 - 1.4\,V_x + 0.06$	186

TABLE 9 (Continued)

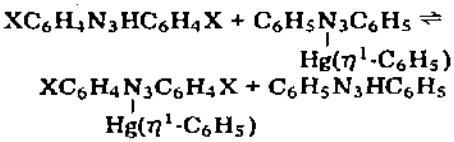
Chemical system	Correlation	Ref.
 $XC_6H_4N_3HC_6H_4X + C_6H_5\underset{\displaystyle Hg(\eta^1\text{-}C_6H_5)}{N}{}_3C_6H_5 \rightleftharpoons XC_6H_4\underset{\displaystyle Hg(\eta^1\text{-}C_6H_5)}{N}{}_3C_6H_4X + C_6H_5N_3HC_6H_5$ X = H, 4-CH_3, 4-OCH_3, 4-F, 3-F	log K/σ	186
$PtH(XC_6H_4N_3C_6H_4X)(PPh_3)_2$ X = 4-Cl, 4-F, H, 4-CH_3	τ(Pt—H) (ppm)/σ J(Pt—H) (ppm)/σ	189
Arylnitrile complexes		
$TiCl_4(NCC_6H_4X)_2$ X = H, 2-CH_3, 2-NH_2, 4-Cl, 3,4-$(C_4H_4)_2$, 4-CN, 2,4-Cl_2, 3-CH_3, 4-CH_3, 4-OCH_3, 4-CN, 4-NO_2, 3-OCH_3, 3-NH_2, 4-NH_2, 3-NO_2, 4-F, 4-$N(CH_3)_2$	$\Delta\nu$(CN) (cm^{-1})/σ	192
$(\eta^5\text{-}C_5H_5)Mn(CO)_2(4\text{-}XC_6H_4CN)$ X = NO_2, CF_3, CN, COC_2H_5, H, CH_3, OCH_3	$\Delta\nu$(CN) (cm^{-1})/σ k_{CO} (mdyne cm^{-1})/σ $\bar{\nu}_{CT}$ (cm^{-1})/σ	193
trans-Mo(diphos)$_2$(N_2)(4-XC_6H_4CN) X = NH_2, OCH_3, CH_3, H, Cl, $COCH_3$	$\nu(N_2)$(cm^{-1})/σ	195
2 *cis*-$[Rh(CO)_2Cl(NCC_6H_4X)] \rightleftharpoons 2\ NCC_6H_4$ + $[RhCl(CO)_2]_2$ X = H, 4-NO_2, 4-OCH_3, 4-$HNCOCH_3$, 4-F	log K/σ $\rho \sim 3.6$ ($CHCl_3$)	196
$(\eta^1\text{-}C_6H_5CH_2)Pd(PEt_3)_2(NCC_6H_4X) \rightleftharpoons (\eta^3\text{-}C_6H_5CH_2)Pd(PEt_3)_2(NCC_6H_4X)$ X = 4-OCH_3, 4-CH_3, H, 4-$COCH_3$	log K/σ $\rho = 1.5$ (CH_2Cl_2)	197
$[(NH_3)_5Co(NCC_6H_4X)]^{3+} + OH^- \rightarrow [(NH_3)_5Co(NHCOC_6H_4X)]^{2+}$ X = 4-OH, H, 3-OH, 4-CN, 3-CN, 4-$COCH_3$, 3-CHO	log k/σ	198, 201
$[(NH_3)_5Co(NCC_6H_4X)]^{3+}$/Cr(II)	log k/σ	201
$[Mo(CO)_2(PBu^n_3)_2(NCC_6H_4X)_2$, $Mo(CO)_2(PPh_3)_2(NCC_6H_4X)_2$ $Mo(CO)_2(PBu^n_3)_3(NCC_6H_4X)$ X = 3-Cl, 3-Br, 4-Cl, 4-Br, H, 3-CH_3, 4-CH_3, 4-OCH_3, 4-NH_2, 4-$N(CH_3)_2$	$\bar{\nu}_{CT}$ (cm^{-1})σ	203
Other ligands with a N donor atom		
$[PdCl_2(Ph_3PNC_6H_4X)]_2$, $[PdCl_2(CH_3CN)(Ph_3PNC_6H_4X)$ X = 4-NO_2, 4-$CO_2C_2H_5$, 4-Cl, H, 4-CH_3, 4-OCH_3	$\Delta\nu$(P=N) (cm^{-1})/σ	205

TABLE 9 (Continued)

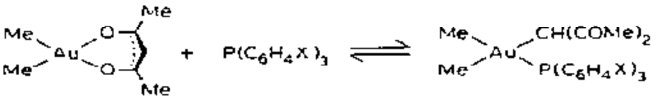
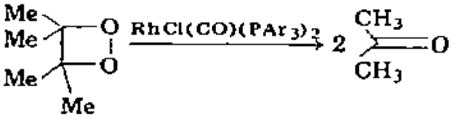
Chemical system	Correlation	Ref.
$TiCl_4 \cdot 2(2,4,6\text{-}Me_3C_6H_2N{=}CHC_6H_4X)$ X = H, 4-CH_3, 4-OCH_3, 4-OH, 4-$N(CH_3)_2$, 4-Cl, 4-Br, 3-Br, 3-NO_2, 4-NO_2	$\nu(CN)/\sigma$ $\Delta H_{mix}/\sigma$ $\rho = -7.8$ (benzene)	206, 207
Aryl phosphines, arsines and stibines $2\ Co(DH)_2(PAr_3) + BrCH_2C_6H_5 \rightarrow BrCo(DH)_2(PAr_3) + (\eta^1\text{-}C_6H_5CH_2)Co(DH)_2(PAr_3)$ Ar = C_6H_4X; X = 4-OCH_3, 4-CH_3, H, 4-Cl	$\log k_2/\sigma$ $\rho = 1.4$ (benzene)	108
$Ni(CO)_3P(C_6H_4X)_3$ X = 2-OCH_3, 4-OCH_3, 2-CH_3, 4-CH_3, 3-CH_3, 4-F, 4-Cl, 3-F, H, 2,3,4,5,6-F_5, 3-Cl	$\nu(CO)(A_1) = 2056.1 + \sum_{i=1}^{3} \chi_i$ (cm^{-1}) $\nu(CO)/\sigma$, Kabachnik's σ	208 209
$Ni(CO)_3P(C_6H_5)_2(C_6H_4X)$ X = 2-OCH_3, 2,4,6-$(CH_3)_3$, 4-OCH_3, 4-F, 3-F, 4-Cl, 2,3,4,5,6-F_5	$\nu(CO)(A_1) = 2056.1 + \sum_{i=1}^{3} \chi_i$ (cm^{-1})	208
$Ni(CO)_3P(OC_6H_4X)_3$ X = H, 2,4-$(CH_3)_2$, 4-CH_3, 4-OCH_3, 2-CH_3, 2-CH_3-4-Cl, 4-Cl, 4-CN	$\nu(CO)(A_1) = 2056.1 + \sum_{i=1}^{3} \chi_i$ (cm^{-1})	208
$Cr(CO)_5P(C_6H_4X)_3$, $Cr(CO)_5As(C_6H_4X)_3$, $Cr(CO)_5Sb(C_6H_4X)_3$ X = H, 4-F, 4-Cl, 3-F, 3-Cl	$\nu(CO)(A_1^{(2)})/\sigma$	212
$(+)\text{-}(\eta^5\text{-}C_5H_5)Mn(NO)(PAr_3)(COC_6H_5) \rightarrow (-)\text{-}(\eta^5\text{-}C_5H_5)Mn(NO)(PAr_3)(COC_6H_5)$ Ar = C_6H_4X; X = 4-CF_3, 4-Cl, 4-F, H, 4-C_6H_5, 4-CH_3, 4-OCH_3, 4-N-$(CH_3)_2$	$\log k/\sigma$ $\rho = 2.14$ (toluene)	214
$RuY_3(NO)(P(C_6H_4X)Et_2)_2$, Y = Cl, Br; X = 4-$N(CH_3)_2$, H, 4-$OCH_3$, 4-Cl	$\nu(Ru{-}Y)$/Taft's σ_p	215
 X = 4-CH_3, 4-OCH_3, H, 4-Cl	$\log K/\Sigma\sigma$ $\rho = -1.6$ $(CDCl_3)$	216
$RhCl(CO)(PAr_3)_2 + TCNE \rightleftharpoons TCNE \cdot RhCl(CO)(PAr_3)_2$ Ar = C_6H_4X; X = 4-OCH_3, 4-CH_3, H, 4-Cl	$\log k_2/\sigma$ $\rho = -2.5$ (acetone)	217
	$\log k/\sigma^+$	218

TABLE 9 (Continued)

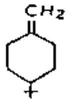
Chemical system	Correlation	Ref.
trans-$IrCl(CO)(PAr_3) + O_2 \rightleftharpoons O_2IrCl(CO)(PAr_3)_2$ Ar = C_6H_4X; X = 4-Cl, H, 4-CH_3, 4-OCH_3, 4-F, 4-Cl, 4-Br	log k_2 or $\Delta H^{\ddagger}/\Sigma\sigma$ $\rho = -2.4$ (chlorobenzene) $\rho = -2.2$ (benzene)	219 219 109
trans-$IrCl(CO)(PAr_3) + AB \rightarrow Ir(A)(B)(Cl)(CO)(PAr_3)_2$ Ar = C_6H_4X; X = 4-OCH_3, 4-CH_3, H, 4-F, 4-Cl AB = H_2, $C_6H_5CH_2Cl$, CH_3I	log k_2/σ $\rho = -0.7$ (benzene); AB = H_2 $\rho = -2.6$ (benzene); AB = $C_6H_5CH_2Cl$ $\rho = -6.4$ (benzene); AB = CH_3I	109
AB = XC_6H_4I; X = H, 4-Br, 4-Cl, 4-CH_3, 3-CH_3, 4-OCH_3	$\rho = +0.6$ (1-methylnaphthalene) log $k_2\Sigma\sigma$ (Kabachnik's σ parameter) $\rho = +0.4$	221
trans-$IrCl(CO)(PAr_3)_2$ Ar = C_6H_4X; X = 4-OCH_3, 4-CH_3, H, 4-F, 4-Cl	ν(Ir—Cl) (cm^{-1})/σ ν(CO) (cm^{-1})/σ	109
cis-$[PdY_2(P(C_6H_4X)Me_2)_2] \rightleftharpoons$ *trans*-$[PdY_2(P(C_6H_4X)Me_2)_2]$ Y = NCO^-, Cl^- or N_3^-; X = 4-OCH_3, 4-CH_3, H, 4-Cl	ΔH, $\Delta S/\sigma$	224, 225
cis-$[PdY_2(P(C_6H_4X)_2Me)_2] \rightleftharpoons$ *trans*-$[PdY_2(P(C_6H_4X)_2Me)_2]$ Y = NCO^-, Cl^- or N_3^-; X = 4-CH_3, H, 4-Cl	ΔH, $\Delta S/\Sigma\sigma$	224, 225
, $H_2/RhCl(CO)(PAr_3)_2$	*cis*/*trans* product ratio/σ	227
Ligands with an O donor atom		
trans-$[PtH(O_2CC_6H_4X)(PEt_3)_2]$ X = 4-NO_2, 4-CN, 4-I, 4-Br, 4-Cl, H, 4-CH_3, 4-OCH_3, 4-$N(CH_3)_2$, 3-NO_2, 3-I, 3-Br, 3-Cl, 3-F, 3-CH_3, 3-$N(CH_3)_2$, 3,5-$(NO_2)_2$, 2,5-$(NO_2)_2$, 2,4,6-$(NO_2)_3$, 2-NO_2, 2-Br, 2-Cl	τ(Pt—H) (ppm)/pK_a, σ $J(^{195}Pt—^{1}H)$/pK_a ν(Pt—H) (cm^{-1})/pK_a	190, 191
cis-$[Co(en)_2(NH_3)(O_2CC_6H_3(OH)X)]^{2+} + H^+ + H_2O \rightarrow$ *cis*-$[Co(en)_2(NH_3)(H_2O)]^{3+} + HO_2CC_6H_3(OH)X$ X = H, 5-SO_3^-, 5-Br, 5-NO_2, 3-NO_2	log k/pK_{OH}	230
$(XC_6H_4CHO)_2Ni(acac)_2$ X = 4-$N(CH_3)_2$, 4-OCH_3, 4-CH_3, H, 4-Cl, 4-Br, 3-Cl, 4-CN, 3-NO_2, 4-NO_2	log $\Delta\nu$ (Hz)/σ^+	232

TABLE 9 (Continued)

Chemical system	Correlation	Ref.
(IMN)PtCl(OC_6H_4X) X = H, 4-Cl, 3,5-Cl_2, 3-NO_2, 4-C_6H_4CHO, 4-NO_2, 2,6-Cl_2, 2,3,4,5,6-F_5, 2,3,4,5,6-Cl_5, 2,4-$(NO_2)_2$	$J(^{195}Pt—^{1}H)/pK_a$	233
$ZnCl_2 \cdot 2\ (C_6H_4X)_3PO$ X = 4-$N(CH_3)_2$, 4-OCH_3, 4-CH_3, H, 4-Br	$\nu(P{=}O)\ (cm^{-1})/\sigma^+$	234
$TiCl_2 \cdot 2\ (C_6H_4X)_3PO$ X = 4-$N(CH_3)_2$, 4-CH_3, H, 4-OCH_3, 4-Cl, 3-Cl, 3-NO_2	$\nu(P{=}O)\ (cm^{-1})/\sigma^+$	235
$ZnCl_2 \cdot 2\ (4\text{-}XC_6H_4COCH_3)$ X = OCH_3, CH_3, H, Cl, NO_2	$\nu(C{=}O)\ (cm^{-1})/\sigma$	236
$TiCl_4 \cdot 2\ (4\text{-}XC_6H_4COCH_3)$ X = OCH_3, CH_3, Cl, NO_2	$\nu(C{=}O)\ (cm^{-1})/\sigma$	236
Ligands with a S, Se or Te donor atom		
(IMN)PtCl(SC_6H_4X) X = 3-CH_3, 4-CH_3, H, 4-NO_2, 4-Cl, 2,3,4,5,6-F_5, 2,3,4,5,6-Cl_5	$J(^{195}Pt—^{1}H)/pK_a$	233
trans-[$Ptpy_2Cl_2$] + 2 $(XC_6H_4)_2S$ → *trans*-[$Ptpy_2(S(C_6H_4X)_2)_2]^{2+}$ + 2 Cl^- X = 4-NH_2, 4-OH, 4-OCH_3, 4-CH_3, H, 4-F, 4-Cl, 4-NO_2	$\log k_2/\Sigma\sigma,\ n^0_{Pt}$	237
trans-[$Ptpy_2Cl_2$] + 2 $(XC_6H_4)S(C_6H_5)$ → *trans*-[$Ptpy_2(S(C_6H_5)(C_6H_4X))_2]^{2+}$ + 2 Cl^-	$\log k_2/\Sigma\sigma,\ n^0_{Pt}$	237
(η^1-XC_6H_4)Hg(SC_6H_4X') + 2,4,6-$(NO_2)_3C_6H_2I$ → (2,4,6-$(NO_2)_3C_6H_2$)SC_6H_4X' + (η^1-XC_6H_4)HgI	$\log k/\sigma$	239
X′ = H; X = 4-CH_3, 3-CH_3, H, 4-Cl, 3-Cl, 2-CH_3, 2,4,6-$(CH_3)_3$	$\rho = -0.97$ (benzene)	
X = H; X′ = 4-CH_3, 3-CH_3, H, 4-Cl, 3-Cl, 2-CH_3, 2,4,6-$(CH_3)_3$	$\rho = -3.7$ (benzene)	
(η^5-C_5H_5)Ni(PBu^n_3)(SC_6H_4X) X = H, 4-CH_3, 4-Cl, 4-$COCH_3$, 4-NO_2	$\tau(C_5H_5)/\sigma$	240
(η^5-C_5H_5)Ni(PBu^n_3)(SeC_6H_4X) X = H, 4-OCH_3, 4-CH_3, 4-Cl, 3-Cl, 3-CF_3, 4-$COCH_3$	$\tau(C_5H_5)/\sigma$	241
(η^5-C_5H_5)Ni(PBu^n_3)(TeC_6H_4X) X = H, 4-OCH_3, 4-CH_3, 4-Cl, 3-CF_3	$\tau(C_5H_5)/\sigma$	241

TABLE 9 (Continued)

Chemical system	Correlation	Ref.
trans-$[PtH(SC_6H_4X)(PPh_3)_2]$ X = 4-NO_2, 4-Br, 4-Cl, 4-F, H, 4-CH_3, 4-OCH_3	ν(Pt—H) (cm^{-1})/σ $J(^{195}Pt—^1H)$ (Hz)/σ	191
$IrY(H)(SC_6H_4X)(CO)(PPh_3)_2$ Y = Cl, Br or I; X = 4-NO_2, 4-Br, 4-Cl, 4-F, H, 4-CH_3, 4-OCH_3	ν(CO) (cm^{-1})/σ	242, 243
trans-$IrY(CO)(PPh_3)_2 + HSC_6H_4X \rightarrow IrY(H)(SC_6H_4X)(CO)(PPh_3)_2$ Y = Cl, Br; X = 4-NO_2, 4-Br, 4-Cl, 4-F, H, 4-CH_3, 4-OCH_3	log k_2/σ ρ = 3.2 (Y = Cl, benzene) ρ = 2.8 (Y = Br, benzene)	243
$[IrY(SC_6H_4X)(SC_6H_3(NO_2)_2)(CO)(PPh_3)]_2$ Y = Cl, Br or I; X = 4-NO_2, 4-Br, 4-F, H, 4-CH_3, 4-OCH_3	ν(CO) (cm^{-1})/σ	245
$[Fe_4S_4(SC_6H_4X)_4]^{2-}/[Fe_4S_4(SC_6H_4X)_4]^{3-}$ X = H, 4-CH_3, 4-$N(CH_3)^+$, NO_2, $N(CH_3)_2$	$E_{1/2}$ (V)/σ ρ = 0.30 (DMF)	247

[a] Contact shift. [b] Rate of N-methyl exchange.

The relative rates of diazotization of a series of *para*-substituted anilines (X = OCH_3, CH_3, H, Cl, NO_2) according to

$$[RuCl(bipy)_2NO]^{2+} + 4\text{-}XC_6H_4NH_2 \rightarrow [RuCl(bipy)_2(N_2C_6H_4X)]^{2+} + H_2O \quad (66)$$

have been observed to decrease as X became more electron withdrawing [175].

Aryl polyazenides

Substituent effects involving a substituted aryldiazenido group, $^-N_2C_6H_4X$ as a ligand have been probed because of its potential relevance to a better understanding of the activation of molecular dinitrogen [176]. Linear correlations have been reported between the position of the band maximum for the $n \rightarrow \pi^*$ transition of the azo group and Hammett's σ parameter for X in the complexes $[Pt(PPh_3)_3(N_2C_6H_4X)]^+$ and $[Pt(PPh_3)_3(N_2HC_6H_4X)]^{2+}$ [177]. The absorption maximum shifts to lower energy as X becomes more electron releasing which suggests that electron delocalization from platinum into the azoaromatic system is not very important. The good correlation for the protonated derivatives supports the conclusion that protonation has occurred at the N=N bond and not at the N atom of the NMe_2 or NEt_2 substituents (see Table 9).

A distinct correlation between the ruthenium $3p_{3/2}$ or $3d_{5/2}$ binding energies and the Hammett σ constant has been recently reported for $RuCl_3$-

$(N_2C_6H_4X)(PPh_3)_2$ complexes which was taken to reflect the presence of substantial "back-bonding" from the metal to the aryldiazenido ligand [178] and to be consistent with a linearly coordinated aryldiazenido ligand [179]. Presumably there is a non-linearly coordinated aryldiazenido ligand in the complexes, $RhCl_2(N_2C_6H_4X)(PPh_3)_2$ (X = 4-NO_2, 4-OCH_3, 4-CH_3) since the rhodium $3d_{5/2,3/2}$ binding energies are essentially insensitive to the nature of X [178]. The ν(N=N) frequency in the Raman for these complexes (X = 4-CF_3, 4-NO_2, 4-F, H, 4-Br, 4-OCH_3 or 4-$N(C_2H_5)_2$) decreases as X becomes a better electron donor [180]. The same trend is observed for the corresponding diazonium salts, $[N_2C_6H_4X]BF_4$, which suggests that the aromatic ring is largely responsible for the π-interaction in these complexes rather than the metal.

For complexes of the type $[IrCl(CO)(PPh_3)_2(N_2C_6H_4X)]BF_4$ and $[IrCl_2(CO)(PPh_3)_2(N_2C_6H_4X)]$, the $n \rightarrow \pi^*$ transition shifts to lower energy as X becomes more electron withdrawing [181]. A weakening of the N=N bond by resonance was confirmed by observing a better linear correlation using "exalted" σ values (which take into account resonance between X and the diazo group) [22] for X = 4-CH_3CO, 4-CN or 4-NO_2.

By contrast however, the ν(N=N) frequency for $[Mo(OH)(CO)_2(N_2C_6H_4X)]_4$ (X = H, 2-Cl, 4-Cl, 4-Br, 2-Br, 2-CH_3) is not sensitive to the nature of X [182]. There is also no systematic variation in ν(N=N) with various substituents in $(\eta^5\text{-}C_5H_5)Cr(CO)_2(N_2C_6H_4X)$ complexes [183] where X = H, 4-OCH_3, 4-CH_3, 4-F, 4-NO_2. However the ν(CO) frequency increases and the chemical shift for the C_5H_5 protons decreases as X becomes more electron withdrawing and as a consequence of these observations the $N_2C_6H_4X$ ligand can be considered to be a three-electron donor in these particular complexes.

The first order rate of N-methyl exchange in a series of seven coordinate aryldiazenidomolybdenum complexes, $Mo(N_2C_6H_4X)(S_2CNMe_2)_3$ increases as X becomes more electron releasing and exhibits a small substituent effect ($\rho = -0.64$) [185]. A better linear least squares fit to σ rather than σ^+ suggests that the effect of X is transmitted via an inductive mechanism only. The potentials of the one electron oxidation of these complexes

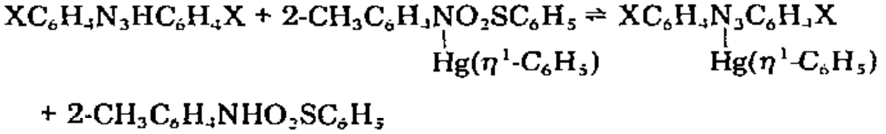
$$Mo(N_2C_6H_4X)(S_2CNMe_2)_3 \rightarrow Mo(N_2C_6H_4X)(S_2CNMe_2)^+ + e^- \qquad (67)$$

also exhibit a good linear correlation with σ [184] but the ^{13}C chemical shifts of the S_2CNMe_2 ligands are insensitive to the nature of X indicating that its effect is not transmitted to these parts of the molecule [185].

The two parameter correlational relationship

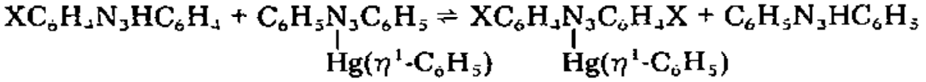
$$\log K = 1.6\,\sigma_o - 1.4\,V_x + 0.06 \qquad (68)$$

where σ_o = the *ortho*-substituent constant [187] and V_x = an *ortho* steric parameter [188], has recently been used to quantify *ortho*-substituent effects for the exchange between a diaryltriazene and 2′-methylbenzenesulphonanilide coordinated to Hg(II) [186].



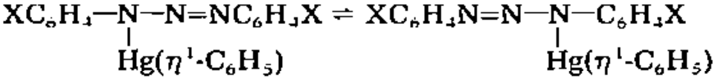
$$XC_6H_4N_3HC_6H_4X + 2\text{-}CH_3C_6H_4\underset{\displaystyle Hg(\eta^1\text{-}C_6H_5)}{N}O_2SC_6H_5 \rightleftharpoons XC_6H_4\underset{\displaystyle Hg(\eta^1\text{-}C_6H_5)}{N_3}C_6H_4X + 2\text{-}CH_3C_6H_4NHO_2SC_6H_5 \qquad (69)$$

A normal Hammett correlation was also reported [186] for the exchange of diaryltriazenes according to



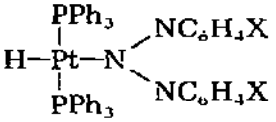
$$XC_6H_4N_3HC_6H_4 + C_6H_5\underset{\displaystyle Hg(\eta^1\text{-}C_6H_5)}{N_3}C_6H_5 \rightleftharpoons XC_6H_4\underset{\displaystyle Hg(\eta^1\text{-}C_6H_5)}{N_3}C_6H_4X + C_6H_5N_3HC_6H_5 \qquad (70)$$

Electron releasing substituents shift the position of equilibrium to the left. These correlations have been used as support for the suggestion that these exchange processes occur in part via a rapid intramolecular metallotropic rearrangement

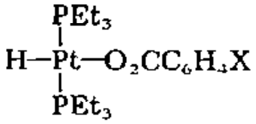


$$XC_6H_4\text{—}\underset{\displaystyle Hg(\eta^1\text{-}C_6H_5)}{N}\text{—}N{=}NC_6H_4X \rightleftharpoons XC_6H_4N{=}N\text{—}\underset{\displaystyle Hg(\eta^1\text{-}C_6H_5)}{N}\text{—}C_6H_4X \qquad (71)$$

The quantities τ(Pt—H) and J(Pt—H) for *trans*-PtH($XC_6H_4N_3C_6H_4X$)-(PPh_3)$_2$ complexes, XXXI, show a linear correlation with σ [189]. A similar result has been reported for *trans*-PtH($O_2CC_6H_4X$)(PEt_3)$_2$, XXXII,

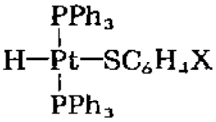


XXXI



$$H\text{—}\overset{\displaystyle PEt_3}{\underset{\displaystyle PEt_3}{Pt}}\text{—}O_2CC_6H_4X$$

XXXII



$$H\text{—}\overset{\displaystyle PPh_3}{\underset{\displaystyle PPh_3}{Pt}}\text{—}SC_6H_4X$$

XXXIII

complexes [190]. However, for *trans*-PtH(SC_6H_4X)(PPh_3)$_2$ complexes, XXXIII, only J(Pt—H) shows a linear correlation with σ; τ(Pt—H) is insensitive to the nature of X [191]. These results again demonstrate the unpredictable nature of correlations involving NMR parameters for structurally similar organometallic compounds.

Arylnitriles

For the complexes, $TiCl_4(NCC_6H_4X)_2$ [192], $\Delta\nu(CN)(\nu(CN)_{\text{coordinated ligand}} - \nu(CN)_{\text{free ligand}})$, has been plotted against the Hammett σ parameters to obtain the empirical relationship given by

$$\Delta\nu(CN) = 2267 + 16.1\,\sigma \qquad (72)$$

which relates the nitrile stretching frequency to the nature of the coordinated nitrile. The ν(CN) frequencies for the series of complexes, (η^5-C_5H_5)Mn(CO)$_2$-

($4\text{-}XC_6H_4CN$) have also been treated in a similar manner [193]. The effect of X also manifests itself in the coordinated CO ligand for these particular manganese complexes since a plot of the force constant, k_{CO} versus σ_p is also linear.

As noted previously, $\Delta\nu$(CN) in the Raman for the platinum(II) complexes, *trans*-$[Pt(CH_3)(PMe_2Ph)_2(NCC_6H_4X)]^+$ is also sensitive to the electronic effect of X [147]. However, it is instructive to note that $\Delta\nu$(CN) in the Raman is insensitive to the nature of the substituent X in a series of six-coordinate iridium(III) complexes, $[IrCl(CO)(PMe_2Ph)_2(CH_3)(NCC_6H_4X)]^+$ (X = $4\text{-}NO_2$, $4\text{-}CH_3$, $4\text{-}OCH_3$ or $2,3,4,5,6\text{-}F_5$) [194].

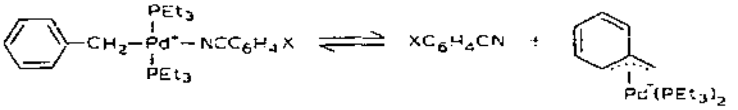
A good correlation has been reported between $\nu(N_2)$ and σ_p for the complexes, *trans*-$[Mo(diphos)_2(N_2)(4\text{-}XC_6H_4CN)]$ [195]. As expected, electron releasing substituents increase the electron density at the metal center which results in a lowering of the $\nu(N_2)$ frequency because of the enhanced metal to N_2 π-bonding.

Equilibrium and kinetic data for arylnitrile metal complexes have also been related to substituent effects. Equilibrium constants for the equilibrium

$$2\,cis\text{-}[Rh(CO)_2Cl(NCC_6H_4X)] \rightleftharpoons 2\ NCC_6H_4X + [RhCl(CO)_2]_2 \qquad (73)$$

have been correlated to σ [196] with $\rho \sim 3.6$ suggesting that the rhodium—nitrile bond is essentially a σ-bond with very little π-bond character.

A good linear free energy relationship between log K and σ_p for the rearrangement of a coordinated benzyl group



(74)

has been observed with $\rho = 1.5$ suggesting that a significant amount of positive charge has been delocalized from palladium to the aromatic nitrile [197].

The linear free energy relationship

$$\log k = 3.89\,\sigma + 1.25 \qquad (75)$$

has been reported for reaction (76) [198]

$$[(NH_3)_5Co(NCC_6H_4X)]^{3+} + OH^- \rightarrow [(NH_3)_5Co(NHCOC_6H_4X)]^{2+} \qquad (76)$$

where X = 4-OH, H or 3-OH. This linear free relationship is not unexpected because similar linear free relationships for the free nitriles have been reported [199,200]. However, Balahura et al. [201] have indicated that this relationship is not quantitative since an incorrect value for one of the σ parameters was used to obtain the correlation. Balahura et al. have further investigated reaction (76) with X = 4-CN, 3-CN, $4\text{-}COCH_3$ and 3-CHO and have concluded that the rate of hydrolysis is sensitive to substitution at the *ortho* and *para* positions of the coordinated nitrile and that the rates of reaction show the expected trend with respect to Hammett's σ constant [201].

The rate of Cr(II) reduction of $[(NH_3)_5Co(NCC_6H_4X)]^{3+}$ has also been correlated to the σ_m and σ_p^- parameters [202].

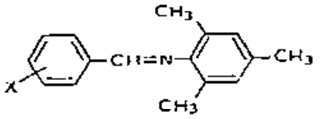
Electronic spectral data for several arylnitrile complexes have been related to substituent effects. The position of the charge transfer band in the complexes, $(\eta^5\text{-}C_5H_5)Mn(CO)_2(NCC_6H_4X)$ [193], $Mo(CO)_2(PBu^n_3)_2(NCC_6H_4X)_2$ [203], $Mo(CO)_2(PPh_3)_2(NCC_6H_4X)_2$ [203], and $Mo(CO)_2(PBu^n_3)_3(NCC_6H_4X)$ [203] correlates linearly with the appropriate Hammett σ parameter. The energy of these particular charge transfer bands increases as X becomes more electron withdrawing which suggests that these electronic transitions are of of the metal-to-ligand type. However, in the ruthenium complexes, $[Ru(NH_3)_5(NCC_6H_4X)]^{2+}$ and $[Ru(NH_3)_5(NCC_6H_4X)]^{3+}$ no simple correlation was detected between the energy of the charge transfer transition in these complexes and the σ parameters [204].

The foregoing correlations are summarized in Table 9.

Other ligands with a nitrogen donor atom

The quantity $\Delta\nu(P{=}N)$, $\nu(P{=}N)_{free} - \nu(P{=}N)_{complex}$, for the iminophosphorane complexes, $[PdCl_2(Ph_3PNC_6H_4X)]_2$ and $[PdCl_2(CH_3CN)(Ph_3PNC_6H_4X)]$, decreases as X becomes more electron withdrawing and it is also a linear function of the Hammett σ parameter indicating that electron releasing substituents strengthen the Pd—N bond in these complexes [205].

The heats of formation [206], ν(CN) [207] as well as the heats of mixing in benzene [208] for the 1 : 2 complexes between $TiCl_4$ and XXXIV are linearly correlated to Hammett's σ parameter for X. The heats of mixing are



XXXIV

very sensitive to changes in the substituent ($\rho = -7.8$) and the negative reaction constant indicates that the $TiCl_4$ moiety is electron-withdrawing.

Aryl phosphines, phosphites, arsines and stibines

Substituent effects originating in an axially coordinated triaryl phosphine in $Co(DH)_2(PAr_3)$ complexes have been studied [108] via eqn. (77).

$$2\,Co(DH)_2(PAr_3) + BrCH_2C_6H_5 \rightarrow BrCo(DH)_2(PAr_3) + (\eta^1\text{-}C_6H_5CH_2)Co(DH)_2(PAr_3) \qquad (77)$$

The second order rate constants exhibit a good linear correlation with the Hammett σ parameters for the substituents, X, with a reaction constant equal to -1.4. This negative reaction constant is consistent with the expectation that the ease of oxidation from Co(II) to Co(III) will be favoured by electron releasing substituents which promote an increase in electron density at the metal center.

The ν(CO) (A_1) mode of $Ni(CO)_3L$ complexes where L = $P(C_6H_4X)_3$ [208,209], $P(C_6H_5)_2(C_6H_4X)$ [208] or $P(OC_6H_4X)_3$ [208] has been used to assess the donor-acceptor properties of L. The effect of X has been defined in terms of

$$\nu(\text{CO})\ (A_1) = 2056.1 + \sum_{i=1}^{3} \chi_i\ \text{cm}^{-1} \tag{78}$$

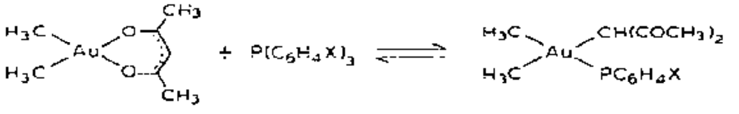
where χ_i is the substituent contribution (arbitrarily set equal to zero for X = t-C_4H_9) [208]. The χ_i values also showed an excellent linear correlation with Kabachnik's σ parameters which are based on the ionization constants in water of a large number of alkyl and aryl substituted phosphorous acids [210,211]. The ν(CO) frequencies have also been directly correlated to Hammett's σ parameter as well as Kabachnik's σ parameter [209]. A similar correlation involving Hammett's σ parameter and the $A_1^{(2)}$ mode for $LCr(CO)_5$ complexes has been reported [212], where L = $P(C_6H_4X)_3$, $As(C_6H_4X)_3$ or $Sb(C_6H_4X)_3$.

It is interesting at this point to note that the ^{31}P chemical shifts for Ni[P-$(OC_6H_4X)_3]_4$ complexes (X = 4-OCH_3, 4-CH_3, 2-CH_3, H, 4-CN) apparently do not show a distinct correlation with the donor-acceptor character of the phosphite as defined by eqn. (78) [213].

It was previously noted that the rate of racemization of (+) or (—)-(η^5-C_5H_5)Mn(NO)(PPh_3)(COC_6H_4X) complexes [113] is more rapid for electron releasing substituents (see page 133). However the rate of racemization of the related derivatives (+) or (—)-(η^5-C_5H_5)Mn(NO)(PAr_3)(COC_6H_5), where Ar = C_6H_4X, decreases as X becomes more electron releasing and shows a good correlation with Hammett's σ parameter [214]. These results are consistent with an S_N1 mechanism for the racemization process.

The ν(Ru—Y) frequency (Y *trans* to NO) in the complexes $RuY_3(NO)$(P-$(C_6H_4X)Et_2)_2$ (Y = Cl or Br) can be correlated to Taft's σ_p parameter. However, the significance of this particular correlation is uncertain since ν(NO) and the other ν(Ru—Y) frequencies do not show any systematic trends as X is varied [215].

The equilibrium constant for the rearrangement of coordinated acetylacetone in the presence of $P(C_6H_4X)_3$



(79)

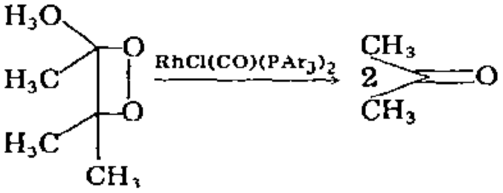
exhibits a linear correlation with $\Sigma\sigma(\rho = -1.6)$ indicating that electron rich phosphines are better nucleophiles in promoting this rearrangement process [216].

Electron releasing substituents on the phenyl ring(s) of aryl phosphines are expected to enhance the basicity of the phosphine which should manifest itself in an increase in electron density at a metal center for a given complex. The following chemical systems adequately illustrate this phenomenon [217—225].

Upon addition of TCNE to *trans*-$RhCl(CO)(PAr_3)_2$

$$RhCl(CO)(PAr_3)_2 + TCNE \rightleftharpoons TCNE \cdot RhCl(CO)(PAr_3)_2 \tag{80}$$

where $Ar = C_6H_4X$, both the rate ($\log k_2$) and the equilibrium constant increase as X becomes more electron releasing [217]. The decomposition of tetramethyl-1,2-dioxetane into acetone is catalyzed by $RhCl(CO)(PAr_3)_2$ complexes [218].



(81)

A firm interpretation of the effect of X in this decomposition is difficult but the rate of decomposition increases as X becomes more electron releasing and it correlates better with σ^+ rather than σ. The "cup-shaped" Hammett plot with σ could be converted into a straight line when the Yukawa-Tsuno equation [6,22] or the Swain-Lupton equation with $\mathcal{F} = 0.116$ and $\mathcal{R} = 0.833$ [21] were fitted to the available data.

The effect that X exerts in the oxidative addition reactions of *trans*-$IrY(CO)L_2$ complexes where Y = Cl, Br or I and $L = P(C_6H_4X)_3$ have been studied by several workers [109,219,220,221]. For the addition of O_2 to this type of iridium(I) substrate

$$IrCl(CO)L_2 + O_2 \underset{k_{-1}}{\overset{k_2}{\rightleftharpoons}} O_2 \cdot IrCl(CO)L_2 \tag{82}$$

where $L = P(C_6H_4X)_3$, Vaska and Chen [219] found that $\log k_2$ (or $\Delta H^{\ddagger}$) could be correlated to the Hammett σ constant according to

$$\log k_2 = 0.194 - 14.1\ \Sigma\sigma \tag{83}$$

The quantities k_2 and k_2/k_{-1} each showed a direct correlation with $(1/\nu(CO))$ for both the substrate and the dioxygen complex. Linear correlations involving $\nu(CO)$ and $\nu(Ir—Cl)$ for $IrCl(CO)L_2$ derivatives have also been reported [109]. Both frequencies decrease as σ becomes less positive reflecting the increased electron density at the metal. Similar results for eqn. (82) have been reported for a more extensive series of substituted phosphines [220]. The rates of addition of H_2, $C_6H_5CH_2Cl$, and CH_3I to $IrCl(CO)L_2$ also correlate with σ giving negative reaction constants [109] (see Table 9) which are consistent with a polar, asymmetric three-centered transition state. The foregoing correlations involving $\log k$ for the various oxidative additions and Hammett's σ parameter can be somewhat improved if the Hammett parameter is replaced by Kabachnik's σ parameter. This modification permits data for alkylarylphosphines to be included in these linear free energy relationships [222].

A recent study [221] has shown that electron withdrawing groups in either the incoming aryl iodide, XC_6H_4I, or substrate, *trans*-$IrCl(CO)(PAr_3)_2$, enhance the rate of reaction (84) and that a two term rate law is obeyed.

$$IrCl(CO)(PAr_3)_2 + XC_6H_4I \rightarrow Ir(Cl)(I)(C_6H_4X)(CO)(PAr_3)_2 \qquad (84)$$

The second order rate constant shows a linear correlation with σ_p for the aryl halide's substituents and Kabachnik's $\Sigma\sigma$ parameter for the phosphines.

Because of small differences in the electronic spectral data for $IrCl(CO)(PAr_3)_2$ complexes ($Ar = C_6H_4X$; X = 2-CH_3, 4-OCH_3, 4-Cl, H, 4-CH_3, or 3-CH_3), no meaningful correlations between the band maxima and the electronic effect of the substituent are possible [223].

Hammett σ constants have also been used as an indicator of phosphine basicity in the following equilibria

$$cis\text{-}[PdY_2(P(C_6H_4X)Me_2)_2] \rightleftharpoons trans\text{-}[PdY_2(P(C_6H_4X)Me_2)_2] \qquad (85)$$

$$cis\text{-}[PdY_2(P(C_6H_4X)_2Me)_2] \rightleftharpoons trans\text{-}[PdY_2(P(C_6H_4X)_2Me)_2] \qquad (86)$$

where $Y = NCO^-$, Cl^-, or N_3^-.

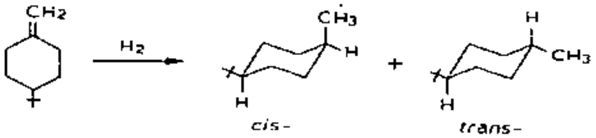
Plots of ΔH, ΔS, versus σ or $\Sigma\sigma$ have been interpreted in terms of the electronic effect of X and the steric effect of Y for a particular phosphine [224,225].

A recent communication [226] reports that the rate of

$$cis\text{-}[PtH(CH_3)(PAr_3)_2] \xrightarrow{k_1} Pt(PAr_3)_2 + CH_4 \qquad (87)$$

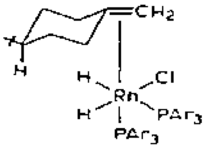
at −25° is dependent on the nature of X; the rate decreases in the order: 4-Cl > H > 4-CH_3 > 4-OCH_3 which parallels the anticipated tendency of the phosphines to stabilize platinum(0) and hence increase the driving force for the production of products.

The *cis*/*trans* product ratios for the catalytic hydrogenation of 1-methylene-4-t-butyl-cyclohexane, eqn. (88) have been studied as a function of σ for

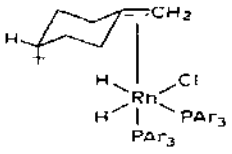


(88)

various substituents, X, in the presence of $RhCl(CO)(P(C_6H_4X)_3)_2$ as catalyst [227]. Both electron-releasing and electron-withdrawing substituents increase the *cis*/*trans* ratios of the products. A non-linear Hammett-type plot is obtained when the *cis*/*trans* ratio is plotted versus Hammett's parameter which has been interpreted in terms of varying degrees of σ and π bonding associated with the metal—olefin bond in those species, XXXV and XXXVI, which lead to the observed products. Similar results were also obtained using $[RhCl(P(C_6H_4X)_3)_2O_2]_2/P(C_6H_6X)_3$ as catalyst.



XXXV



XXXVI

Ligands with an O donor atom

The quantities $\tau(Pt—H)$, $J(^{195}Pt—^1H)$ from the ^1H NMR spectra and the $\nu(Pt—H)$ frequency from the IR spectra of a number of *trans*-$PtH(O_2CC_6H_4X)(PEt_3)_2$ derivatives [190] each show a good linear correlation with the pK_a of the corresponding $HO_2CC_6H_4X$ acid. These correlations have been interpreted in terms of variations in bond strength, the amount of *s*-character, and bond distance for the Pt—H bond as a consequence of the electronic effects exerted by the various substituents.

There is no correlation between the position of the amide I band (ca. 1650 cm^{-1}) in the IR and Hammett's σ parameter for a series of octahedral nickel(II) and cobalt(II) complexes containing substituted benzamides as ligands, $[M(H_2NCOC_6H_4X)_6](ClO_4)_2$ (M = Ni or Co; X = 4-OCH_3, 4-CH_3, H, 4-Cl or 4-NO_2) [228]. This result is not unreasonable in view of the fact that this particular band is not a pure $\nu(C{=}O)$ mode but is coupled with other vibrations.

There is also no apparent simple relationship between the rate of the solvolysis reaction

$$trans\text{-}[Co(en)_2(O_2CC_6H_4X)_2]^+ + HO_2CCH_3$$
$$\rightarrow trans\text{-}[Co(en)_2(O_2CC_6H_4X)(O_2CCH_3)]^+ + HCO_2C_6H_4X \qquad (89)$$

and the nature of the substituent (X = H, 2-CH_3, 3-CH_3, 4-CH_3, 2,3-$(CH_3)_2$, 2,4-$(CH_3)_2$, 2,5-$(CH_3)_2$, 3,4-$(CH_3)_2$ or 3,5-$(CH_3)_2$) [229].

The rate of aquation in aqueous perchlorate medium [230] as well as the rate of base hydrolysis [231] of *cis*-(ammine)bis(ethylenediamine)(substituted salicylato)cobalt(III) have been studied as a function of the nature of the substituent and the rates of aquation have been correlated to the pH_{OH} for the coordinated carboxylato ligand [230].

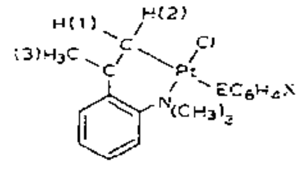
$$cis\text{-}[Co(en)_2(NH_3)(O_2CC_6H_3(OH)X)]^{2+} + H^+ + H_2O$$
$$\rightarrow cis\text{-}[Co(en)_2(NH_3)(H_2O)]^{3+} + HO_2CC_6H_3(OH)X \qquad (90)$$

$$cis\text{-}[Co(en)_2(NH_3)(O_2CC_6H_3(OH)X)]^{2+} + OH^-$$
$$\rightarrow cis\text{-}[Co(en)_2(NH_3)(OH)]^{2+} + {}^-O_2CC_6H_3(OH)X \qquad (91)$$

where X = H, 5-SO_3^-, 5-Br, 5-NO_2 or 3-NO_2.

There is a linear relationship between the observed isotropic shift, log $\Delta\nu$ (Hz), of the aldehydic proton for a series of substituted benzaldehydes and Hammett's σ^+ parameter for 1 : 2 complexes with $Ni(acac)_2$ [232]. The interaction between the two aldehyde molecules and the metal center is weak but $\Delta\nu$ (Hz) increases as σ^+ becomes more positive (increasing acidity of the aldehydic proton) suggesting that there is a partial positive charge delocalized over the substituent, aromatic ring and the exocyclic carbon atom.

The basicity of substituted phenolates in XXXVII has been studied [233]



XXXVII E = O
XXXVIII E = S

utilizing the observed linear plots of $J[^{195}Pt—^1H(1)]$, $J[^{195}Pt—^1H(2)]$ and $J[^{195}Pt—^1H(3)]$ versus the pK_a for the appropriate phenol, HOC_6H_4X. All three sorts of coupling constants increased as the pK_a increased. The slopes of these plots as well as the magnitude of the coupling constants are larger than the corresponding values for the analogous thiophenolate derivatives, XXXVIII, indicating that there is some π-acidity associated with the thiophenolato ligands.

The $\nu(P{=}O)$ frequency for a series of adducts, $ZnCl_2 \cdot 2\ (C_6H_4X)_3PO$ [234] and $TiCl_4 \cdot 2\ (C_6H_4X)_3PO$ [235] show a better correlation with the σ^+ parameter than the σ parameter in agreement with the acceptor character of the metal centers. These particular linear correlations are given in eqns. (92) and (93) respectively.

$$\nu(P{=}O) = 1157 + 13.3\ \Sigma\sigma^+ \qquad r = 0.994 \tag{92}$$

$$\nu(P{=}O) = 1126 + 15.6\ \Sigma\sigma^+ \qquad r = 0.996 \tag{93}$$

The corresponding correlations for the $ZnCl_2 \cdot 2$ L and $TiCl_4 \cdot 2$ L adducts (L = a 4-substituted acetophenone) are given by

$$\nu(C{=}O) = 1609 + 37\sigma \qquad r = 0.998 \tag{94}$$

$$\nu(C{=}O) = 1565 + 61\sigma \qquad r = 0.999 \tag{95}$$

where $\nu(C{=}O)$ is corrected for resonance with the 8a and 8b benzene frequencies [236]. As expected, the presence of a phosphorus atom diminishes the electronic effect of X. It is also noteworthy that the above correlations were obtained using data obtained in the solid state.

Ligands with a S, Se, or Te donor atom

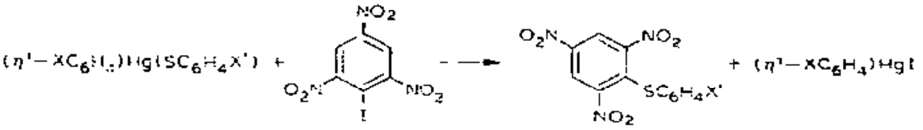
The nucleophilicity of symmetrically and unsymmetrically substituted diphenyl sulfides towards platinum(II) has been studied [237].

$$trans\text{-}[PtCl_2py_2] + 2(XC_6H_4)_2S \rightarrow trans\text{-}[Ptpy_2(S(C_6H_4X)_2)_2]^{2+} + 2\,Cl^- \qquad (96)$$

$$trans\text{-}[PtCl_2py_2] + 2(XC_6H_4)S(C_6H_5)$$
$$\rightarrow trans\text{-}[Ptpy_2(S(C_6H_4X)(C_6H_5))_2]^{2-} + 2Cl^- \qquad (97)$$

Plots of log k_2 versus $\Sigma\sigma_p$ were linear and have been used to rationalize the inability of 4,4′-dinitrodiphenyl sulfide to coordinate to Pt(II). A similar plot is obtained when log k_2 is plotted versus the appropriate nucleophilic reactivity constant, n^0_{Pt} [238].

Electron donating substituents associated with XC_6H_4 or SC_6H_4X' enhance the rate of



(98)

The reaction constants $\rho = -0.97$ and $\rho = -3.67$ obtained from plots of log k versus σ for X (X′ = H) and X′ (X = H) respectively are consistent with a proposed four center transition state for this particular reaction [239].

Plots of $\tau(C_5H_5)$ versus σ for a number of $(\eta^5\text{-}C_5H_5)Ni(PBu^n_3)(M'C_6H_4X)$ derivatives (M′ = S, Se or Te) are linear with slopes of −17.9 for M′ = S [240], −18.7 for M′ = Se [241], and −19.3 for M′ = Te [241] indicating that the electronic effect of M′ is transmitted to the cyclopentadienyl ring in these particular compounds. Unfortunately, no unambigous conclusions regarding the nature of the Ni—M′ bond can be reached from these data alone.

Substituent effects associated with the reactivity of substituted arenethiols towards Pt(0) [191] and Ir(I) [242—244] have been studied.

$$Pt(PPh_3)_{4-n} + HSC_6H_4X \rightarrow trans\text{-}[PtH(SC_6H_4X)(PPh_3)_2] + 2-n\ PPh_3 \qquad (99)$$

$n = 0$ or 1

$$IrY(CO)(PPh_3)_2 + HSC_6H_4X \rightarrow IrY(H)(SC_6H_4X)(CO)(PPh_3)_2 \qquad (100)$$

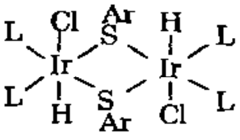
Y = Cl, Br or I

$$2\,IrCl(PPh_3)_3 + 2\,HSC_6H_4X \rightarrow [IrHCl(SC_6H_4X)(PPh_3)_2]_2 + 2\,PPh_3 \qquad (101)$$

The values of ν(Pt—H) and $J(^{195}$Pt—H) increase as X becomes more electron withdrawing for the complexes, $PtH(SC_6H_4X)(PPh_3)_2$ [191]. Plots of these quantities versus the σ parameter of X are linear confirming the *trans* configuration for these complexes and serve to demonstrate that the electronic effect of X is reflected in the Pt—H bond. However, there is no correlation between τ(Pt—H) and σ for these particular complexes whereas τ(Pt—H) is a linear function of σ for the similar carboxylato derivatives, $PtH(O_2CC_6H_4X)(PEt_3)_2$ [190]. The reason for this difference is not readily apparent.

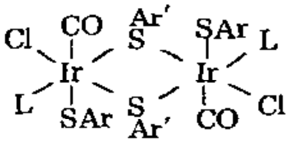
Linear correlations between ν(CO) and Hammett's σ parameter have been observed for the products of reaction (100) and have been used to determine their stereochemistry [242,243]. The rate of oxidative addition of HSC_6H_4X to $IrY(CO)(PPh_3)_2$ (Y = Cl, Br) also exhibits a good correlation with σ and increases with increasing acidity of the incoming thiol [243] which is consistent with the notion that the intimate mechanism involves an initial approach by the H of the thiol towards the metal center.

For the complexes $[IrHCl(SC_6H_4X)(PPh_3)_2]_2$, XXXIX, the lack of a correlation between ν(Pt—H) and Hammett's σ parameter for X suggests a *cis* arrangement of the hydride and arenethiolate ligands [244].



XXXIX

L = PPh_3



XL

L = PPh_3

The electronic effect exerted by various X groups in 2,4-$(NO_2)_2C_6H_3SSC_6H_4X$

$$2[IrY(CO)(PPh_3)_2] + 2\ ArSSAr' \rightarrow [IrY(SAr)(SAr')(CO)(PPh_3)]_2 + 2\ PPh_3 \qquad (102)$$

where Y = Cl, Br or I; Ar = C_6H_4X and Ar' = 2,4-$(NO_2)_2C_6H_3$, has been used to acquire structural information about the product of reaction as well as mechanistic information [246,247]. The linear plot of ν(CO) versus σ for X is consistent with the presence of a CO ligand *trans* to SAr, XL [245]. Since the rate of reaction is insensitive to the nature of X, the initial step in the mechanism of this reaction involves attack at the metal center by the sulfur atom which is bonded to the 2,4-dinitrophenyl group [246].

As noted above, correlations involving the $J(^{195}Pt—^{1}H)$ values for H(1), H(2) and H(3) with pK_a data for the complexes XXXVIII lead to the conclusion that there is some π-acidity associated with the sulfur atoms [233].

The addition of one electron to the tetranuclear cluster complex, $[Fe_4S_4(SC_6H_4X)_4]^{2-}$ to form $[Fe_4S_4(SC_6H_4X)_4]^{3-}$ has been shown to be sensitive to the nature of X; the redox potential, $E_{1/2}$ becomes more positive as X becomes more electron withdrawing and is linearly correlated with the σ parameters of the substituents [247].

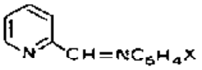
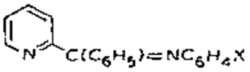
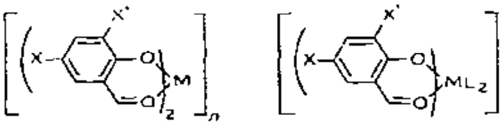
(ii) Bidentate and polydentate ligands

Ligands with N donor atoms

For the complexes, $Ni(PEt_3)_2(XC_6H_4N{=}NC_6H_4X)$, a correlation between the shift in the position of the $n \rightarrow \pi^*$ electronic transition of the diazene ligand upon coordination versus the Hammett σ parameter has been observed. The difference, $\Delta\lambda_{max}$ becomes larger as X becomes more electron

TABLE 10

Summary of correlations involving polydentate ligands with N-donor atoms

Chemical system	Correlation	Ref.
$Ni(PEt_3)_2(XC_6H_4N{=}NC_6H_4X)$ X = 4-F, H, 4-CH_3, 4-OC_2H_5, 4-NH_2	$\Delta\lambda_{max}(n \rightarrow \pi^*)/\sigma$	248
$Ni(NCBu^t)(XC_6H_4N{=}NC_6H_4X')$ X,X′ = 4-NH_2, H; 4-OCH_3, 4-OCH_3; H,H; 4-NO_2, H; 3,5-$(CH_3)_2$, 3,5-$(CH_3)_2$; 4-CH_3, 4-CH_3; 4-NO_2, 4-NO_2	ν(CN) (cm^{-1})/$\Sigma\sigma$	120
$Cu(P2A{-}C_6H_4X)_2/[Cu(P2A{-}C_6H_4X)]^+$ X = 4-NO_2, 4-$COCH_3$, 4-$CO_2C_2H_5$, 4-CF_3, 4-Cl, 4-Br, 4-I, 4-F, 4-C_6H_5, H, 4-CH_3, 4-OCH_3, 4-$N(CH_3)_2$	$E_{1/2}$ (V)/σ^0	251
$[FeL_3]^{2+}/H^+$, $[FeL_3]^{2+}/OH^-$ L =  X = 4-CH_3, 4-F, 4-Cl, 4-Br, 4-OH, 4-OCH_3, 3-CH_3, 3-Cl, 3-OH, 3-OCH_3	log k/σ	252, 254
$[FeL_3]^{2+}/H^+$ L =  X = 4-Cl, 4-F, 3-Cl, H, 4-CH_3, 3-CH_3, 3,4-$(CH_3)_2$, 3-OCH_3, 3,5-$(CH_3)_2$	log k/σ	253
 M = Co(II), Ni(II), Cu(II) X, X′ = H, H; H, Cl; I, I; Br, Br; Cl, Cl; OCH_3, H	ν(M—O) (cm^{-1})/$\sigma_p - \sigma'$	273
$TiCl_4 \cdot (C_6H_5)_2P(O)CH_2C(O)C_6H_4X$ X = 4-OCH_3, 4-CH_3, H, 4-Cl, 4-Br, 2,4-$(CH_3)_2$, 2,4,6-$(CH_3)_3$	ν(C=O) (cm^{-1})/σ^+	274
$[Ni(S_2C_2(C_6H_4X)_2)_2] + e^- \rightleftharpoons [Ni(S_2C_2(C_6H_4X)_2)_2]^-$ $[Ni(S_2C_2(C_6H_4X)_2)_2]^- + e^- \rightleftharpoons [Ni(S_2C_2(C_6H_4X)_2]$ X = H, 4-OCH_3, 4-CH_3, 4-Cl	$\Delta E_{1/2}$[a] (V)/$\Sigma\sigma^*$ [b] (slope = 1.40, CH_3CN)	275
$Mo(CO)_5(XC_6H_4SC_2H_4SC_6H_4X) \rightarrow Mo(CO)_4(XC_6H_4SC_2H_4SC_6H_4X) + CO$ X = H, 4-CH_3, 4-OCH_3, 4-$N(CH_3)_2$	$\log(k_X/k_H)/\sigma$ (ρ = −0.25, n-nonane)	276

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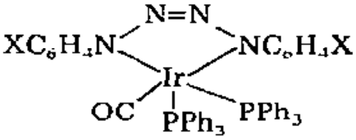
[a] $\Delta E_{1/2} = E_{1/2}(X) - E_{1/2}(CH_3)$. [b] σ^* for the aryl substituents was converted to the aliphatic scale by adding 0.60.

withdrawing and this has been related to the stability of these complexes in solution [248].

The isocyanide ν(CN) frequencies for the complexes, [Ni(CNBu^t)$_2$-(XC$_6$H$_4$N=NC$_6$H$_4$X')](X = X or X ≠ X', see Table 10) [120] have been correlated to Hammett's σ parameters for the substituents. The slope of the plot of ν(CN) versus $\Sigma\sigma$ is smaller than that observed for the analogous complexes containing a substituted styrene (see page 136).

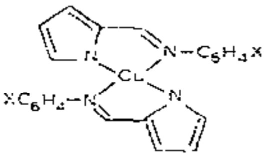
The ν(CO) frequency increases with increasing value of σ for X in the series of complexes, XLI (X = H, 4-F, 4-Cl, 4-Br, 4-CF$_3$ or 4-OCH$_3$) which contain a substituted aryl tetrazene ligand [249]. However, this trend is not linear which is probably due to the fact that the IR data were obtained in the solid state.



XLI

The relative rate of the catalytic *cis—trans* isomerization of the diazenes, XC$_6$H$_4$N=NC$_6$H$_4$X' (X, X' = Cl, H; Cl, Cl; H, H; CH$_3$, H; OCH$_3$, H or CH$_3$, CH$_3$) in the presence of (η^5-C$_5$H$_5$)$_2$MoH$_2$ shows a small dependence on the nature of X and tends to increase as X becomes more electron withdrawing [250].

Remote substituent effects have also been studied for complexes XLII [251] using the Cu(II)/Cu(I) redox couple as a probe for these effects. A



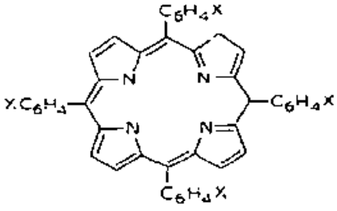
XLII

plot of $E_{1/2}$ (V) versus Taft's σ^0 substituent parameter is linear with $\rho = 0.076$ V which is similar to that observed for complexes having a substituted tetraphenylporphyrin ligand (vide infra). It should be noted that the ESR parameters for this particular series of complexes are apparently insensitive to the nature of X.

Burgess and his co-workers have noted several unorthodox Hammett correlations involving the rate of acid fission of a number of [Fe(N-(2-pyridylmethylene)substituted aniline)$_3$]$^{2+}$ [252] and [Fe(α-(2-pyridylbenzylidene)-substituted aniline)$_3$]$^{2+}$ [253] complexes as well as the rate of base fission of [Fe(N-(2-pyridylmethylene)substituted aniline)$_3$]$^{2+}$ [254] complexes. Better linear correlations were obtained when log (k_x/k_H) for a complex having a *para*-substituted ligand was plotted versus σ_m rather than σ_p. The converse correlation was observed for the *meta*-substituted complexes. No satisfactory explanation for these observations is yet available. That there is no satisfactory Hammett correlation for the rate of reaction of CN^- with $[Fe(\alpha\text{-}(2\text{-pyridylbenzylidene})\text{substituted aniline})_3]^{2+}$ has been ascribed to the fact that the cyanide attack occurs at the metal center whereas the σ constants are related to a property of the ligands [255].

Substituted tetraphenylporphyrins

Hammett correlations involving metalloporphyrin complexes containing a substituted tetraphenylporphyrin (XTPP), XLIII, have been obtained using equilibrium data [256–263], electrochemical data [264–268], kinetic data [270,271] and electronic spectral data [272].



XLIII

Equilibrium constants involving a four, five or six-coordinate substituted TPP complex and a base such as piperidine [256,257], N-methylimidazole [258,259], pyridine [257,260,261,262] or molecular oxygen [257,263] have been shown to obey the Hammett relation

$$\log(K_X/K_H) = 4\,\sigma\rho \tag{103}$$

These particular systems are summarized in Table 11. The ρ values fall within a small range and are usually positive indicating that adduct formation is favoured by electron withdrawing substituents which reinforce a positive charge at the metal center. However, there appears to be no clear cut systematic trend with respect to the sign and magnitude of these reaction constants. For instance, a negative reaction constant is observed for Fe(III) [258,260], a zero reaction constant for Co(III) [261] and a positive reaction constant for Fe(II) [260,261]. The nature of the solvent also affects the sign of ρ [257, 261]. The negative reaction constants observed with O_2 as incoming ligand [257,263] are consistent with the electrophilic character of dioxygen in these reactions.

The effect of substituents in the electrode processes, eqns. (104–(107) have been studied where M = VO^{2+} [264], Fe(II) [264,265,266], Co(II) [257,264,267], Ni(II) [257,268], Cu(II) [264], or Zn(II) [264]

$$[M(XTPP)] + e^- \rightleftharpoons [M(XTPP)]^- \tag{104}$$

$$[M(XTPP)]^- + e^- \rightleftharpoons [M(XTPP)]^{2-} \tag{105}$$

$$[M(XTPP)] \rightleftharpoons [M(XTPP)]^+ + e^- \tag{106}$$

$$[M(XTPP)]^+ \rightleftharpoons [M(XTPP)]^{2+} + e^- \tag{107}$$

TABLE 11

Summary of correlations involving substituted tetraphenylporphyrin complexes

Chemical system	Correlation	Ref.
Ni(4-XTPP) + 2 pip ⇌ Ni(pip)$_2$(4-XTPP)	log $\beta_2/4\sigma$ ρ = 0.33 (toluene)	256
Ni(3-XTPP) + 2 pip ⇌ Ni(pip)$_2$(3-XTPP)	log $\beta_2/4\sigma$ ρ = 0.41 (toulene)	
4-X=OCH$_3$, CH$_3$, H, F, Cl, CO$_2$CH$_3$, CN, NO$_2$		
3-X=OCH$_3$, CH$_3$, H, F, Cl, CN, NO$_2$		
VO(4-XTPP) + pip ⇌ VO(pip)(4-XTPP)	log $K/4\sigma$ ρ = 0.11 (toluene)	256
X = OCH$_3$, CH$_3$, H, Cl, CN		
FeCl(4-XTPP) + 2 N—MeIm ⇌ [Fe-(N—MeIm)$_2$(4-XTPP)]$^+$Cl$^-$	log $\beta_2/4\sigma$ ρ = −0.39 (CHCl$_3$) ρ = −0.41 (CHCl$_3$)	258 259
X = OCH$_3$, CH$_3$, H, F, Cl		
Fe(DMF)$_2$(3 or 4-XTPP)$^+$Cl$^-$ + 2 py ⇌ 2 DMF + Fe(py)$_2$(3 or 4-XTPP)$^+$Cl$^-$	log $K/4\sigma$ ρ = −0.43 (DMF)	260
X = OCH$_3$, CH$_3$, H, F, Cl		
Fe(DMF)$_2$(3-XTPP)$^+$Cl$^-$ + py ⇌ Fe(DMF)(py)-(3-XTPP)$^+$Cl$^-$ + DMF	log $K/4\sigma$ ρ = −0.12 (DMF)	260
Fe(DMF)$_2$(4-XTPP)$^+$Cl$^-$ + py ⇌ Fe(DMF)(py)-(4-XTPP)$^+$Cl$^-$ + DMF	log $K/4\sigma$ ρ = −0.45 (DMF)	
3-X = 4-X = OCH$_3$, CH$_3$, H, F, Cl		
Fe(DMF)$_2$(3 or 4-XTPP) + 2 py ⇌ 2 DMF + Fe(py)$_2$(3 or 4-XTPP)	log $\beta_2/4\sigma$ ρ = 0.13 (DMF) ρ = 0.09 (DMSO)	260 261
X = OCH$_3$, CH$_3$, H, F, Cl		
Co(4-XTPP) + py ⇌ Co(py)(4-XTPP)	log $K/4\sigma$ ρ = 0.1 (toluene)	257
X = OCH$_3$, CH$_3$, H, F, Cl, CN, NO$_2$	ρ = 0.16 (DMSO)	261
Co(4-XTPP) + pip ⇌ Co(pip)(4-XTPP)	log $K/4\sigma$ ρ = 0.15 (toluene)	257
X = OCH$_3$, CH$_3$, H, Cl, CN, NO$_2$		
Co(py)(4-XTPP) + O$_2$ ⇌ Co(py)(O$_2$)(4-XTPP)	log $K/4\sigma$ ρ = −0.11 (toluene)^a	257
X = OCH$_3$, CH$_3$, H, F, Cl, CN, NO$_2$		
[Co(DMSO)$_2$(4-XTPP)]$^+$ + py ⇌ [Co(DMSO)(py)(4-XTPP)]$^+$ + DMSO	log $K_1/4\sigma$ ρ = 0 (DMSO)	261
[Co(DMSO)$_2$(4-XTPP)]$^+$ + 2 py ⇌ [Co(py)$_2$(4-XTPP)]$^+$ + 2 DMSO	log $K_2/4\sigma$ ρ = 0 (DMSO)	
X = OCH$_3$, CH$_3$, H, Cl, CN		
Mn(py)(4-XTPP) + O$_2$ ⇌ Mn(O$_2$)(4-XTPP) + py	log $K/4\sigma$ ρ = −0.41 (toluene)^b	261
Mn(4-XTPP) + O$_2$ ⇌ Mn(O$_2$)(4-XTPP)	ρ = 0.08 ^{c}	
X = OCH$_3$, CH$_3$, H, F, Cl		
Zn(3 or 4-XTPP) + py ⇌ Zn(py)(3 or 4-XTPP)	log $K/4\sigma$ ρ = 0.19 (benzene)	262
X = OCH$_3$, CH$_3$, F, Cl, H		
[M(4-XTPP)] + e$^-$ ⇌ [M(4-XTPP)]$^-$	$E_{1/2}$ (V)/4σ	257,

TABLE 11 (Continued)

Chemical system	correlation	Ref.
$[M(4\text{-}XTPP)]^- + e^- \rightleftharpoons [M(4\text{-}XTPP)]^{2-}$ $[M(4\text{-}XTPP)] \rightleftharpoons [M(4\text{-}XTPP)]^+ + e^-$ $[M(4\text{-}XTPP)]^+ \rightleftharpoons [M(4\text{-}XTPP)]^{2+} + e^-$ M = VO^{2+}, Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) X = OCH_3, CH_3, H, F, Cl, CO_2CH_3, CN or NO_2	$\rho = 0.07$ V[d]	264—268
$[M(XTPP)]^+ + e^- \rightleftharpoons [M(XTPP)]$ $[M(XTPP)]^{2+} + e^- \rightleftharpoons [M(XTPP)]^+$ $[M(XTPP)]^{3+} + e^- \rightleftharpoons [M(XTPP)]^{2+}$ $[M(XTPP)]^- + e^- \rightleftharpoons [M(XTPP)]^{2-}$ M = Co(III); X = 4-OCH_3, 4-CH_3, H, 4-F, 4-Cl, 4-CN, 4-NO_2 M = Fe(I), Fe(II) or Fe(IV); X = 3-CN, 4-CN, 4-CO_2CH_3, 3-Br, 3-Cl, 3-F, 3-$OCH_2C_6H_5$, 4-Cl, 4-F or H	$E_{1/2}$ (V)/4σ $\rho = 0.07$ V[d]	257, 266
Fe(N—MeIm)$_2$(4-XTPP) + N—MeIm* $\rightleftharpoons$ Fe(N—MeIm)(N—MeIm*)(4-XTPP) + N—MeIm X = Cl, H, CH_3, OCH_3	$1/\tau$ (s^{-1})/4σ[e]	269
Ru(CO)(t-Bupy)(4-XTPP) + t-Bupy* $\rightleftharpoons$ Ru(CO)(t-Bupy*)(4-XTPP) + t-Bupy X = CF_3, Cl, H, CH_3, i-C_3H_7, OCH_3, 4-$N(C_2H_5)_2$	$1/\tau$ (s^{-1})/4σ $\rho = -0.17$ (1,1,2,2-tetrachloroethane)	270
$CuCl_2$ + 4-$XTPPH_2$ $\rightleftharpoons$ Cu(4-XTPP) + 2 HCl	$\Delta G^{\ddagger}$/4σ $\Delta\nu$ (cm^{-1})[f]/($\sigma^+ - \sigma$)	272

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[a] $T = 72°C$, $\rho = -0.093$ at $-56.5°C$ and -0.82 at $-38°C$. [b] $T = -78°C$. [c] Estimated value of ρ. [d] Average value of ρ in CH_2Cl_2. [e] Taft's parameter. [f] Q band (π—π^* transition) for complex — Q band (π—π^* transition) for free ligand.

as well as the electrode processes, eqns. (108)—(111) where M = Co(III) [257], Fe(I), Fe(III) or Fe(IV) [266]

$$[M(XTPP)]^+ + e^- \rightleftharpoons [M(XTPP)] \tag{108}$$

$$[M(XTPP)]^{2+} + e^- \rightleftharpoons [M(XTPP)]^+ \tag{109}$$

$$[M(XTPP)]^{3+} + e^- \rightleftharpoons [M(XTPP)]^{2+} \tag{110}$$

$$[M(XTPP)]^- + e^- \rightleftharpoons [M(XTPP)]^{2-} \tag{111}$$

The Hammett relation, eqn. (103), is obeyed for most of these processes and the appropriate reaction constants, ρ (V) have been calculated in several non-aqueous solvents (see Table 11). The reaction constants are normally positive and do not appear to be directly affected by the overall charge on the complex or the formal oxidation state of the central metal [264]. In general, the $E_{1/2}$ values shift to a more cathodic potential as the substituents become more electron donating or in other words, electron substituents render oxidation more easy. However, the detailed mechanisms of these electrode reactions remain to be clarified.

It is interesting to note that as observed for Cu(P2A—$C_6H_4X)_2$ complexes [251], the ESR parameters for VO(4-XTPP) and VO(pip)(4-XTPP) complexes [256] are also insensitive to the nature of X.

Various other types of measurements have been used to correlate substituent effects in TPP complexes. These are also summarized in Table 11. The rate of axial exchange [269] in a series of complexes of the type Fe(N—MeIm)$_2$(4-XTPP)$^+$Cl$^-$ has been correlated with Taft's σ parameter using ^{1}H NMR wide line spectroscopy. The variation in rate parallels that observed for the equilibrium constant data [258] and increases as X becomes more electron donating.

The effect of phenyl ring substituents on the rate of 4-tert-butylpyridine exchange with Ru(CO)(t-Bupy)(4-XTPP) complexes has been studied; the rate increases as the substituent becomes more electron donating which is consistent with the presence of a more basic porphyrin [270]. There also is a linear correlation between the rate of exchange and Hammett's σ parameter. However, the rate of phenyl ring rotation in these particular complexes as well as TiO(4-XTPP) complexes (X = CF_3, Cl, CH_3, i-C_3H_7, OCH_3, OH, $N(C_2H_5)_2$) [272] does not show a linear correlation with the σ parameter.

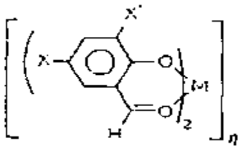
The free energy of activation for the binding of Cu(II) by various TPP ligands, in DMF

$$CuCl_2 + 4\text{-XTPPH}_2 \rightarrow Cu(4\text{-XTPP}) + 2\ HCl \qquad (112)$$

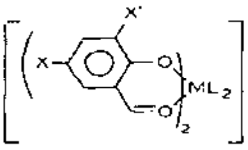
shows a better correlation with σ^+ than σ [272]. A linear correlation was also noted between $\Delta\nu$ and $(\sigma^+ - \sigma)$ but not with σ or σ^+ separately where $\Delta\nu$ = the Q band of the complex $-Q$ band of the free ligand at 7511 cm^{-1} which may be interpreted in terms of mainly an inductive effect due to the various X substituents.

Ligands with O or S donor atoms

The ν(M—O) vibration in the substituted salicylaldehyde derivatives XLIV and XLV where M = Co(II), Ni(II) or Cu(II) and L = H_2O or py [273] have been correlated to Taft's resonance polar parameter, $\sigma_p - \sigma'$ [168]. The



XLIV



XLV

dependence of ν(M—O) on a resonance rather than an inductive parameter suggests that metal—ligand π bonding may play an important role in stabilizing these particular complexes.

The ν(C=O) frequencies for a series of complexes, $TiCl_4 \cdot (C_6H_5)_2P(O)CH_2C(O)C_6H_4X$ [274] have been correlated to the σ^* parameter via

$$\nu(C{=}O) = 1569 + 72\sigma^* \tag{113}$$

and increase as X becomes more electron withdrawing.

The potentials for the one and two electron reductions

$$[Ni(S_2C_2(C_6H_4X)_2)_2] + e^- \rightleftharpoons [Ni(S_2C_2(C_6H_4X)_2)_2]^- \tag{114}$$

$$[Ni(S_2C_2(C_6H_4X)_2)_2]^- + e^- \rightleftharpoons [Ni(S_2C_2(C_6H_4X)_2)_2]^{2-} \tag{115}$$

show a linear correlation with Taft's inductive parameter, σ^* [168] with a slope equal to 1.40 [275]. This suggests that substituent effects are essentially inductive in these nickel complexes.

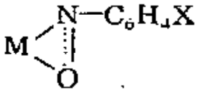
The Hammett plot of $\log(k_X/k_H)$ versus σ for

$$Mo(CO)_5(XC_6H_4SC_2H_4SC_6H_4X) \rightarrow Mo(CO)_4(XC_6H_4SC_2H_4SC_6H_4X) + CO \tag{116}$$

yields a reaction constant, $\rho = -0.25$ [276] which indicates that electron donation to the reaction site promotes chelation. However, no significant substituent effect is apparent for the ν(CO) frequencies. Table 10 summarizes the correlations involving chelating ligands with O or S donor atoms.

Nitrosoarenes

Relatively few examples of metal complexes containing a coordinated nitrosoarene ligand have been reported. Hence, few systematic data regarding the effect of substituents are available. It has been suggested that for complexes of the type, $[Fe(CO)_3(4\text{-}XC_6H_4NO)]_n$, $n = 1$ when σ for X is negative and $n = 2$ when σ for X is positive or equal to zero [277]. However, this suggestion has been negated by Mossbauer [278] and X-ray diffraction studies [279,280] which indicate that all of these complexes are dimeric regardless of the nature of the substituent. Otsuka and co-workers have noted the absence of any correlation between the ν(NO) frequency and the nature of X in a series of nickel complexes, $[Ni(CNBu^t)_2(4\text{-}XC_6H_4NO)]$ (X = $N(CH_3)_2$, CH_3O, CH_3, H, Cl or Br) [281]. However, each of the IR active A' and A'' modes for ν(CN) gave good linear correlations with σ which are consistent with a *cis*-configuration of ligands about nickel. Consequently, the *cis*-stretch—stretch interaction, $[\nu(CN)(A') - \nu(CN)(A'')]$ also shows a linear correlation with σ. The notion that a considerable amount of electron density is transferred from the metal to the isocyanide ligands is supported by the fact that ν(CN) decreases as X becomes more electron donating. The above data are also consistent with the nitrosoarene ligand being bonded to the metal in a dihapto manner, XLVI. This particular series of complexes has been extended to include the substituents, 4-$N(C_2H_5)_2$, 4-$CO_2C_2H_5$, 3,4-Cl_2 and 2,3,4,5,6-F_5 by Ittel [120] who also noted the correlation between the A' mode and $\Sigma\sigma$.



XLVI

Cyclic voltammetry in acetonitrile has been used to study the reversible one electron reduction

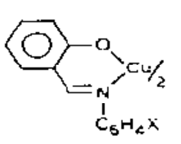
$$[RuCl(bipy)_2(4\text{-}XC_6H_4NO)]^{2+} + e^- \rightleftharpoons [RuCl(bipy)_2(4\text{-}XC_6H_4NO)]^+ \qquad (117)$$

Hammett plots of $E_{1/2}$ versus σ_R, σ_R^0 and $\sigma_p - \sigma_m$ were linear and a reaction constant, $\rho = 1.05$ was noted with σ_R indicating that the redox potential is very sensitive to the nature of X [282]. Since these correlations involve parameters which measure pure resonance effects, the effect of X is presumably transmitted to the metal center via the π-electron system of the nitrosoarene.

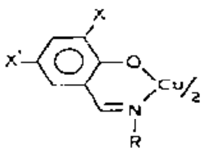
Schiff bases

Schiff base complexes are very amenable to the study of the substituent effects by virtue of the fact that a substituent or substituents can be introduced at a phenyl ring associated with either the aldehyde or amine portion of the ligand. Correlations involving this sort of complex are summarized in Table 12 and are discussed below.

The assignment of the ν(Cu—N) frequencies in the N-arylsalicylaldimine complexes, XLVII, was confirmed by observing a linear correlation between these frequencies and Hammett's σ parameter [283]. The ν(Cu—N) frequencies increase as X becomes more electron withdrawing which is in agreement with the expectation that such substituents will promote Cu—N π-bonding and thereby increase the Cu—N bond strength [284]. Electronic spectral data



XLVII



XLVIII

for a number of bis(N-(alkyl)-substituted salicylaldiminate)copper(II) complexes, XLVIII (R = C_2H_5, i-C_3H_7 or t-C_4H_9; X = H or CH_3 and X' = F, Cl, Br, I, NO_2, CH_3 or OCH_3) have also been interpreted in terms of additional π-bonding between the metal and the ligand [285]. The ν(M—N) frequencies follow the electron releasing capacities of the substituents expressed as $\sigma_p - \sigma'$ [168] for the complexes XLIX and L [286] except for the combination, X, X' = H, Cl (see Table 12).

TABLE 12

Summary of correlations involving polydentate ligands with mixed donor atoms

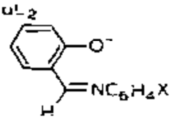
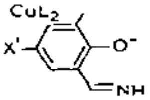
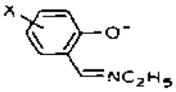
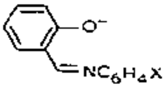
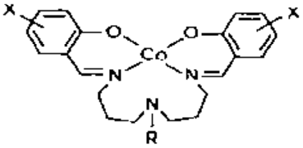
Chemical system	Correlation	Ref.
Nitrosoarene complexes		
$[Fe(CO)_3(4\text{-}XC_6H_4NO)]_n$ X = OCH_3, CH_3, H, Cl, CO_2CH_3	n/σ	277—280
$Ni(CNBu^t)_2(XC_6H_4NO)$ X = 4-$N(CH_3)_2$, 4-$N(C_2H_5)_2$, 4-OCH_3, 4-CH_3, H, 4-Cl, 4-Br, 4-$CO_2C_2H_5$, 3,4-Cl_2, 2,3,4,5,6-F_5	$\nu(CN)\ (A')\ (cm^{-1})/\sigma,\ \Sigma\sigma$ $\nu(CN)\ (A'')\ (cm^{-1})/\sigma$ $[\nu(CN)\ (A') - \nu(CN)\ (A'')]\sigma$	281, 120
$[RuCl(bipy)_2(4\text{-}XC_6H_4NO)]^{2+}/[RuCl\cdot(bipy)_2(4\text{-}XC_6H_4NO)]^+$ X = $N(CH_3)_2$, $NHCH_3$, OH, Br, H, CH_3, NO_2	$E_{1/2}$ (V)/σ_R, σ_R^0, $\sigma_p - \sigma_m$ (ρ = 1.05 with σ_R, CH_3CN)	282
Schiff base complexes		
CuL$_2$ L =  X = 4-OC_6H_5, 4-OCH_3, 4-OC_2H_5, 4-CH_3, 4-C_2H_5, 4-C_6H_5, H, 4-F, 4-Cl, 4-Br, 4-I, 4-$CO_2C_2H_5$, 4-$COCH_3$, 4-CN	$\nu(Cu—N)\ (cm^{-1})/\sigma$	283
CuL$_2$ L =  X, X′ = H, Cl; I, I; Br, Br; Cl, Cl; OCH_3, H	$\nu(Cu—N)\ (cm^{-1})/\sigma_p - \sigma'$	286
CuL_2 + py ⇌ $pyCuL_2$	$\log K/\sigma_p$	290
 X = OCH_3, CH_3, H, F, Cl, Br, I, NO_2	ρ = 1.2	
 X = 4-CH_3, H, 4-Cl, 4-I, 4-CN	ρ = 0.97	290
		

TABLE 12 (Continued)

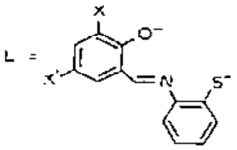
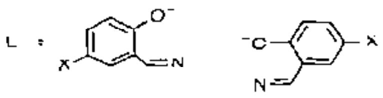
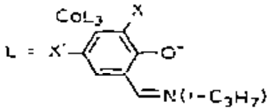
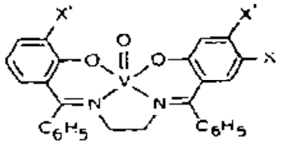
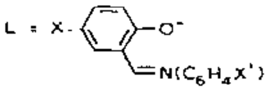
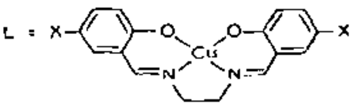
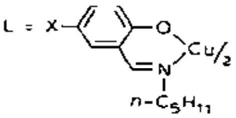
Chemical system	Correlation	Ref.
R = CH_3; X = H, 5-Br, 5-Cl, 3,5-I_2, 3,5-Cl_2, 3,5-Br_2 R = H, X = 5-NO_2, 3-NO_2, H, 5-CH_3, 5-Cl, 3,5-I_2, 3,5-Br_2, 3,5-Cl_2	$E_{1/2}$ (V)/σ_m	291
$Cu^{2+} + NiL \rightarrow CuL + Ni^{2+}$ L =  X X' Cl H H Cl H H H CH_3 H OCH_3 OCH_3 H	log *k*/σ	293
L =  X = Cl, H, CH_3, OCH_3	log *k*/σ	293
L =  X, X' = H, H; H, Cl; I, I; Br, Br; Cl, Cl; OCH_3, H	ν(Co—N) (cm^{-1})/$\sigma_p - \sigma'$	286
 X, X' = H, H; Cl, H; Cl, CH_3; CH_3, H	ν(VO) (cm^{-1})/σ (N_{xy}^2) [a]/σ	287
$CuL_2 + {}^{64}Cu(O_2CCH_3)_2py \rightleftharpoons {}^{64}CuL_2 + Cu(O_2CCH_3)_2py$ L = 	log *k*/$\sigma_{p,m}$	288
X = CH_3; X' = H, 4-Cl, 4-OCH_3, 4-$N(CH_3)_2$, 4-NO_2, 5-NO_2	$\rho = -1.0$, (CH_2Cl_2, −20.0°C)	
X = H; X' = H, 3-F, 3-Cl, 3-CH_3, 3-NO_2, 4-F, 4-Cl, 4-Br, 4-I, 4-CN, 4-NO_2, 4-CH_3	$\rho = +0.32$, (CH_2Cl_2, −20.0°C)	
L =  X = OCH_3, CH_3, H, Cl	$\rho = 1.52$, (CH_2Cl_2, +40.0°C)	288

TABLE 12 (Continued)

Chemical system	Correlation	Ref.
		
X = OCH_3, CH_3, Cl, Br, I, NO_2	$\rho = -1.3$, ($CHCl_3$, 0.0°C)	289
Other ligands $Ni(CNBu^t)(4\text{-}XC_6H_4N{=}C(CF_3)_2)$ X = OCH_3, CH_3, H, Cl	ν(CN) (cm^{-1})/σ	120

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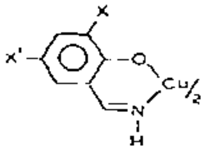
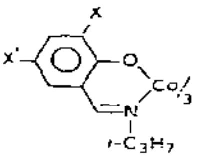
[a] N_{xy}^2 is the coefficient of the d_{xy} AO in the plane MO which contains the unpaired electron.

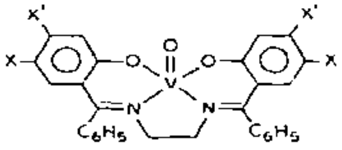


XLIX



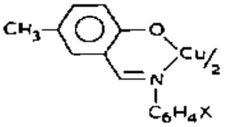
L

The IR ν(V=O) frequency as well as the ESR hyperfine splittings for L have been linearly correlated to Hammett's σ parameter for the various substituents [287]. The ν(V=O) frequency decreases while the hyperfine splittings increase as the substituents become more electron withdrawing.

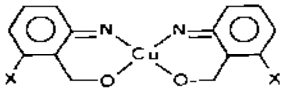


LI

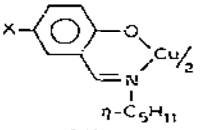
The rates of isotopic copper exchange in CH_2Cl_2 for LII [284], LIII [288], LIV [288] and LV [289] show good linear correlations with Hammett's σ parameter.



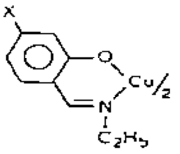
LII



LIII



LIV



LV.

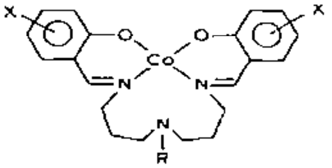
The variations in the magnitude and sign of the various reaction constants (see Table 12) suggest that cleavage of the Cu—O bond is rate determining in the exchange process and that it is probably initiated by attack of residual water at the Cu—O bond [290].

The equilibrium constants for

$$CuL_2 + py \rightleftharpoons pyCuL_2 \qquad (118)$$

can also be correlated to Hammett's σ parameter where CuL_2 = XLVII or LV [290].

A linear correlation between $E_{1/2}$ for the Co^{2+}/Co^{3+} couple and $\Sigma\sigma_m$ for the ring substituents has been reported for LVI where R = CH_3 or H (see Table 12). This suggests that the electronic effect of the substituents are transmitted to the metal via the azomethine group [291].

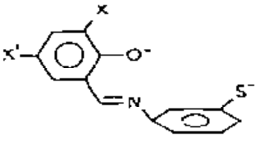


LVI

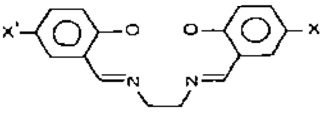
Plots of log k versus σ for reaction (119) in DMSO

$$Cu^{2+} + NiL \rightarrow CuL + Ni^{2+} \qquad (119)$$

where L = LVII or LVIII have been interpreted in terms of a dissociative mechanism for the tridentate ligand and an associative mechanism for the tetradentate ligand [293].



LVII

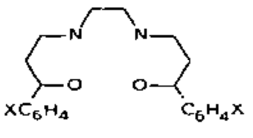


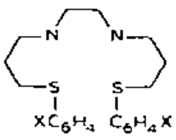
LVIII

Variations in the equilibrium constants for the oxygenation reaction

$$CoLpy + O_2 \rightleftharpoons O_2CoLpy \qquad (120)$$

where L = LIX or LX (X = H, 4-CH_3, 4-OCH_3, 4-Br or 4-Cl) are not readily rationalized in terms of Hammett-Taft parameters [294].


LIX

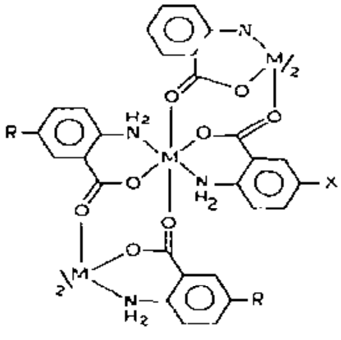

LX

This behaviour is in contrast to that observed when L = a substituted TPP ligand [257] and it has been suggested that this difference may be due to more pronounced π-interactions with LIX and LX as ligands [294].

Other ligands with mixed donor atoms

The isonitrile ν(CN) frequencies of the imine complexes, $Ni(CNBu^t)_2(4\text{-}XC_6H_4N{=}C(CF_3)_2)$ [120] show a linear correlation with Hammett's σ parameter and are affected by X to about the same extent as the diazene complexes, $Ni(CNBu^t)_2(XC_6H_4N{=}NC_6H_4)$ (see page 166).

The shifts in the ν(M—O) and ν(M—N) frequencies have been discussed in terms of Taft's inductive parameter, σ' [168] for LXI [294] where M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and X = Cl, Br, I, H, CH_3. The ν(M—O) frequencies decrease as X becomes more electron withdrawing whereas the ν(M—N) frequencies increase suggesting that the electronic effects of X stabilize the M—O bond at the expense of M—N bonding.


LXI

E. CORRELATIONS INVOLVING STABILITY CONSTANT DATA

(i) Ligands with a C donor atom

The formation constants for 1 : 1 complexes between a substituted benzene and Ag(I) decrease as the substituent becomes more electron withdrawing and a plot of log K versus σ_m is linear ($\rho = -1.60$). If σ_p is used rather than σ_m, a less satisfactory correlation is obtained [295]. The extended form of the Hammett equation (123) has also been applied to the equilibrium, eqn. (121)

$$XC_6H_5 + Ag^+ \rightleftharpoons (\eta^6\text{-}XC_6H_5)Ag^+ \tag{121}$$

$$XC_6H_4CH{=}CH_2 + Ag^+ \rightleftharpoons (\eta^2\text{-}XC_6H_4CH{=}CH_2)Ag^+ \qquad (122)$$

$$\log K_x = \alpha\sigma_I + \beta\sigma_R + \log K_0 \qquad (123)$$

where X = OCH_3, $COCH_3$, $CO_2C_2H_5$, F, Cl, Br, H or CH_3 [296].

A good Hammett correlation for 1 : 1 complexes between Ag(I) and a substituted styrene has been reported with $\rho = -0.77$ [297]. The negative reaction constants for (121) and (122) are consistent with the electrophilic behaviour of Ag(I) in these processes.

A theoretical interpretation of these correlations using simple molecular orbital theory has also been reported [298].

More recently a Hammett-Yukawa relationship has been applied to the 1 : 1 complexes formed on silica gel between Ag(I) and $XC_6H_4CH{=}CH_2$ where X = 4-OCH_3, 4-CH_3, H, 3-OCH_3, 3-Cl or 3-NO_2 [299] and a ρ value of -0.8 was obtained. This compares favourably with the value obtained by direct solubility and distribution experiments [297].

(ii) Ligands with a N or As donor atom

For the equilibrium given by

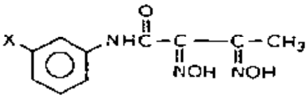
$$Ag^+ + 2\, H_2NC_6H_4X \rightleftharpoons [Ag(H_2NC_6H_4X)_2]^+ \qquad (124)$$

where X = H, 2-CH_3, 2-Br, 2-Cl, 3-NO_2, 3-Cl, 3-Br, 3-CH_3, 4-CH_3, 4-Cl, 4-Br or 4-NO_2, the formation constant, determined in 50% aqueous ethanol, increases as X becomes more electron releasing [300].

Thermodynamic arguments making use of stability and ionization constants have been used to define a so-called stabilization factor, S_f, which provides a measure of the variations in stability of metal complexes formed with a particular series of substituted aromatic ligands [301]. A linear correlation between S_f and Hammett's σ parameter has been reported for the silver-aniline complexes, $[Ag(H_2NC_6H_4X)_2]^+$ which yields a slope equal to 2.2 indicating that an electron withdrawing substituent favours the complexation process [302], a result which is in marked contrast to that noted previously [300].

Stability constants for the Cu(II) chelates formed with substituted *o*-phenylenediamines show a linear correlation with $(\sigma_m + \sigma_p)$ suggesting that both inductive and mesomeric effects are operative in these chelates [303].

The average stability constants for the Co(II) chelates with 2,3-dioximes of *meta*-substituted acetanilides, LXII, are a linear function of the pK_b for the corresponding free aniline [304]. However, no linear relationships were observed when X occupied a *para*-position on the phenyl ring. It is not readily apparent why this difference should be observed.



LXII

Linear Hammett plots between σ and the stability constants for $[AgL]^-$, $[AgHL]$, and $[AgH_2L]^+$ species ($L = XC_6H_4As(CH_2CO_2H)_2$) have been reported [305] with approximate ρ values of −0.8, −1.0, and −0.9 respectively. These reaction constants are comparable to those obtained for analogous sulfur and selenium ligands [306,307] suggesting that the substituent effect is the same for these different donor atoms. The negative ρ values have also been interpreted in terms of the absence of "back-bonding" from Ag to As [305].

(iii) Ligands with an O, S, or Se donor atom

The stability constants for $[Cu(O_2CC_6H_4X)]^+$ are linearly correlated to Hammett's σ constant with $\rho = 0.58$ [308]. The quantity S_f [301,302] also shows a linear correlation with σ for both $[Cu(O_2CC_6H_4X)]^+$ and $[Cu(O_2CC_6H_4X)_2]$ with $\rho = 1.5$ and 1.2 respectively [302]. These correlations were initially taken to imply the presence of metal—ligand π-bonding [307,308] but this interpretation has been challenged [309] with the suggestion that polynuclear species in solution must also be considered.

More recently, Hepler and co-workers' treatment of the Hammett equation [310—312] has been used to predict free energy changes for the formation of $[Cu(O_2CC_6H_4X)]^+$ in solution where X = 3-Cl, 3-Br or 3-I and $[Fe(OC_6H_4X)]^{2+}$ where X = 4-Cl, 4-NO_2, 3-NO_2, 4-Br, 3-Cl, 3-Br [313].

The stability constants for CuL_2 complexes, where L = 2-hydroxy-4- or 5-substituted acetophenone, increase as the substituent becomes more electron releasing and a plot of $\log \beta$ versus pK_a of the ligand is linear [314]. Also, the difference in the free energy change, $\Delta\Delta G$, is a linear function of Hammett's σ parameter where $\Delta\Delta G = \Delta G$ for a substituted acetophenone — ΔG for the unsubstituted acetophenone.

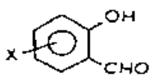
A plot of the stability constants for 1 : 1 complexes of Zn^{2+} with a (±)-α-di(carboxymethyl)amino-α-substituted phenylacetic acid, $4\text{-}XC_6H_4CH(CO_2H)N(CH_2CO_2H)_2$, versus σ is linear with $\rho = -0.65$ [315]. A slope of the same magnitude but opposite sign is obtained from the plot of $\log K$ versus pK_3 of the free ligand. A series of general equations have been developed to assist in the rationalization of these particular data as well as other related linear free energy relationships (LFER) involving metal complexes in solution [316].

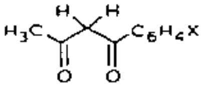
Variations in $\log K_1$ for $[CuL]^+$ complexes where L = LXIII have also been discussed in terms of the linear relationship, eqn. (125) [317,318]

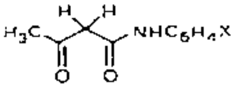
$$\log K_1 = a pK + 6 \qquad (125)$$

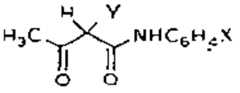
which has been shown to be an oversimplification.

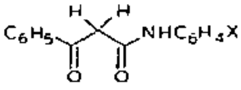
Plots of $\log K_1$, $\log K_2$ or $\log K_{av}$ versus the pK_a (or pK_b) for the ligand have been reported for LXIV coordinated to Ni(II) [319], LXV coordinated to Co(II) [304,320], Ni(II) [320], Cu(II) [320,321,322] and Zn(II) [304], LXVI coordinated to Cu(II) [323], and LXVII coordinated to Cu(II) [321].


LXIII


LXIV


LXV


LXVI Y = Cl
LXVII Y = Br
LXVIII Y = I


LXIX

Since correlations involving a stability constant and the pK_a (or pK_b) of the ligand and Hammett's σ parameter are intrinsically the same [316], it is not surprising that plots of log K_1 or log K_2 versus σ are also linear for LXV [324], LXVIII [325] and LXIX [326] coordinated to Cu(II). For LXI the stabilization factor, S_f, also shows a linear correlation with σ [326].

Linear Hammett plots have been reported for [AgL], $[AgHL]^+$, and $[AgL_2]^-$ where L = $XC_6H_4SCH_2CO_2H$ [306] or $XC_6H_4SeCH_2CO_2H$ [307]. Since the ρ values from these plots are essentially the same whether S or Se is the donor atom (see Table 13), it has been concluded that there is very little, if any, "back-bonding" from Ag to the ligand in these complexes [307]. The observed trends in ΔG, ΔH, and ΔS as a function of X also lend support to the notion that the Ag—L bond in these complexes is essentially a σ-bond [327].

For a series of related complexes, [AgL] where L = an alkyl-substituted benzoic acid, 4-$RC_6H_4CO_2H$, log K_{AgL} is a linear function of Taft's inductive parameter, σ^*, with a slope equal to -0.2 suggesting that there is no π-bonding between the metal and the ligand in these complexes [328].

F. CONCLUDING REMARKS

From the above, it is quite apparent that Hammett-type correlations have been applied to a diverse number of organometallic systems although the number of such correlations is significantly less than those reported for organic chemical systems. Very often the correlations for the organometallic systems do not involve equilibrium or kinetic data upon which the Hammett equation and its extensions are based. In fact, the correlations reported to date are about equally distributed between those which are based on kinetic or equilibrium data and those which are not.

The majority of those correlations involving kinetic or equilibrium data have been interpreted in an analogous manner to that employed for similar organic chemical systems. The presence of a metal center normally diminishes the observed substituent effect. Unfortunately however, the presence of a metal center and/or other factors such as the lack of precise data, the improper choice of substituent parameter, or the lack of sufficiently different substitu-

TABLE 13

Summary of correlations involving stability constant data

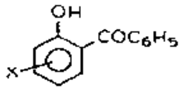
Chemical system	Correlation	Ref.
Ligands with a C donor atom		
$XC_6H_5 + Ag^+ \rightleftharpoons [(\eta^6\text{-}XC_6H_5)Ag]^+$	$\log K/\sigma_m$ $\rho = -1.6$ (H_2O)	295
X = OCH_3, COC_2H_5, $CO_2C_2H_5$, F, Cl, Br, I, NO_2, 1,4-Cl_2, 1,4-Br_2, 1,4-I_2, H, CH_3, OH	$\log K/(\sigma_I, \sigma_R)$	296
$XC_6H_4CH{=}CH_2 + Ag^+ \rightleftharpoons [(\eta^2\text{-}C_6H_4CH{=}CH_2)Ag]^+$ X = 4-CH_3, 4-OCH_3, H, 4-Cl, 3-NO_2, 3-Cl, 3-OCH_3, 3-CH_3	$\log K/\sigma$ $\rho = 0.77$ (H_2O)	297
Ligands with a N or As donor atom		
$Ag^+ + 2\ H_2NC_6H_4X \rightleftharpoons [Ag(H_2NC_6H_4X)_2]^+$ X = 3-CH_3, 4-CH_3, 3-NO_2, 4-NO_2, 3-Cl, 4-Cl, 4-I	S_f/σ $\rho' = 2.2$ (H_2O)	302
$Cu^{3+} + 2\ o\text{-}(H_2N)_2C_6H_3X \rightleftharpoons [Cu(o\text{-}(H_2N)_2C_6H_4X)_2]^{2+}$ X = 4-OCH_3, 4-CH_3, H, 4-CO_2H, 4-Cl	$\log \beta_2/(\sigma_m + \sigma_p)$	303
Co(II)/3-$XC_6H_4NHCOC(NOH)C(NOH)CH_3$ X = OCH_3, 3-Cl, 3-CH_3	$\log K_{av}/pK_b$	304
$Ag^+ + L^{2-} \rightleftharpoons [AgL]^+$	$\log K_{AgL}/\sigma$ $\rho = -0.8$ (H_2O)	305
$Ag^+ + HL^- \rightleftharpoons [AgHL]^+$	$\log K_{AgHL}/\sigma$ $\rho = -1.0$ (H_2O)	305
$Ag^+ + H_2L \rightleftharpoons [AgL]^+$	$\log K_{AgH_2L/\sigma}$ $\rho = -0.9$ (H_2O)	305
$H_2L = XC_6H_4As(CO_2H)_2$; X = 4-$OCH_3$, 4-$CH_3$, H, 3-$OCH_3$, 3-$CH_3$, 4-Cl		
Ligands with an O, S, or Se donor atom		
$Cu^{2+} + XC_6H_4CO_2^- \rightleftharpoons [Cu(O_2CC_6H_4X)]^+$	$\log K_1/K_0 = \sigma\rho$ $\rho = -0.58$ (aq. dioxane)	308
X = H, 3-F, 3-Cl, 3-Br, 3-I, 4-F, 4-Cl, 4-Br, 4-I, 4-t-C_4H_9, 3-t-C_4H_9, 4-OH, 3-OH, 3-NO_2, 4-NO_2, 4-CH_3, 4-OCH_3	S_f/σ $\rho' = 1.5$	312
$Cu^{2+} + 2\ XC_6H_4CO_2^- \rightleftharpoons [Cu(O_2CC_6H_4X)_2]$	S_f/σ $\rho' = 1.2$	312
$Cu^{2+} + 2L \rightleftharpoons CuL_2$	$\log \beta/pK_a$ (aq. dioxane)	314
L = 	$\Delta G_x - \Delta G_0 = 2.303\ RT\rho\sigma_x$	
X = 4-OCH_3, 4-CH_3, H, 4-Cl, 4-Br, 4-NO_2, 5-OCH_3, 5-CH_3, 5-Cl, 5-Br, 5-NO_2		
Zn(II)/4-$XC_6H_4CH(CO_2H)N(CH_2CO_2H)_2$	$\log K_1/\sigma$ $\rho = 0.65$ (H_2O)	315
X = Cl, CH_3, OCH_3, H	$\log K_1/pK_3$	

TABLE 13 (Continued)

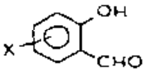
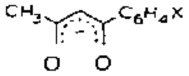
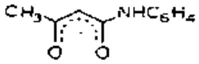
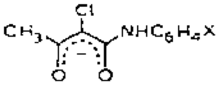
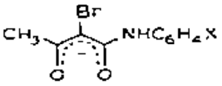
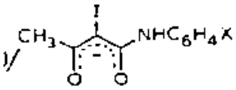
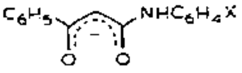
Chemical system	Correlation	Ref.
Cu(II)/ 	$\log K_1 = a\mathrm{p}K + b$	317, 318
X = H, 3-Cl, 5-Cl, 3-OCH$_3$, 5-OCH$_3$, 4-NO$_2$, 3,5-Cl$_2$, 3,5-I$_2$, 4-Cl, 5-Cl, 5-CH$_3$, 4-OCH$_3$, 3-NO$_2$, 5-NO$_2$, 3,5-Br$_2$, 3,5-(NO$_2$)$_2$		
Ni(II)/ 	$\log K_1$, $\log K_2/\mathrm{p}K_a$	319
X = 4-OCH$_3$, 4-CH$_3$, H, 4-F, 4-Cl, 4-Br, 4-I, 4-NO$_2$		
Co(II), Ni(II), Cu(II), Zn(II)/ 		
X = H, 2-CH$_3$, 2-OCH$_3$, 2-Cl, 2,5-Cl$_2$	$\log K_1/\mathrm{p}K_a$ [a]	320
X = H, 4-OCH$_3$, 3-OCH$_3$, 2-OCH$_3$, 2-CH$_3$, 3-CH$_3$, 4-CH$_3$, 2-Cl, 3-Cl, 4-Cl, 3-NO$_2$, 4-NO$_2$	$\log K_1$, $\log K_2$, $\log K_{av}/\mathrm{p}K_b$ [b]	304, 321
X = H, 4-OCH$_3$, 4-CH$_3$, 4-F, 4-Cl, 4-Br, 4-I, 4-CO$_2$C$_2$H$_5$, 4-NO$_2$, 4-CN	$\log K_1$, $\log K_2$, $\log K_{av}/\mathrm{p}K_b$ [b]	322 324
X = 4-NO$_2$, 3-NO$_2$, 3-Cl, 3-OCH$_3$, 3-CH$_3$, 4-CH$_3$	$\log (K_x/K_0) = \rho\sigma$ $\rho = 0.80$ (H$_2$O)	
Cu(II)/ 	$\log K_1$, $\log K_2$, $\log K_{av}/\mathrm{p}K_b$ [b]	323
X = 4-OCH$_3$, 4-CH$_3$, 3-CH$_3$, 4-Cl, 3-Cl, H		
Cu(II)/ 	$\log K_1$, $\log K_2$, $\log K_{av}/\mathrm{p}K_b$ [b]	321
X = 4-OCH$_3$, 4-CH$_3$, 4-Cl, 3-Cl, H		
Cu(II)/ 	$\log (K_x/K_0) = \rho\sigma$	325
X = H, 2-CH$_3$, 3-CH$_3$, 4-CH$_3$, 2-Cl, 3-Cl, 4-Cl, 2,5-Cl$_2$, 2-OCH$_3$		
Cu(II)/ 	$\log \beta_1 = 7.20 - 1.44\,\sigma$ S_f/σ $\rho' = -2.1$ (aq. EtOH)	326
X = 4-OCH$_3$, 4-CH$_3$, 3-CH$_3$, H, 3-OCH$_3$, 4-Cl, 3-Cl, 3-Br, 4-CO$_2$C$_2$H$_5$		

TABLE 13 (Continued)

Chemical system	Correlation	Ref.
$Ag^+ + L^- \rightleftharpoons AgL$ $Ag^+ + HL \rightleftharpoons [AgHL]^+$ $Ag^+ + 2\ L^- \rightleftharpoons [AgL_2]^-$ $HL = XC_6H_4SCH_2CO_2H$; X = H, 2-CH_3, 4-CH_3, 2-OCH_3, 3-OCH_3, 4-OCH_3, 2-Cl, 3-Cl, 4-Cl, 2-CO_2H, 3-CO_2H, 4-CO_2H, 2-NO_2, 4-NO_2, 3-CF_3, 4-CN, 4-Br, 4-NH_2, 2-SCH_3, 4-SCH_3	$\log K_{AgL}/\sigma\ \rho = -0.86$ (H_2O) $\log K_{AgHL}/\sigma\ \rho = -0.67$ (H_2O) $\log K_{AgL_2}/\sigma\ \rho = -0.6$ (H_2O)	306
$Ag^+ + L^- \rightleftharpoons AgL$ $Ag^+ + HL \rightleftharpoons [AgHL]^+$ $Ag^+ + 2\ L^- \rightleftharpoons [AgL_2]^-$ $HL = XC_6H_4SeCH_2CO_2H$; X = H, 2-CH_3, 3-CH_3, 4-CH_3, 2-Cl, 3-Cl, 4-Cl, 2-OCH_3, 3-OCH_3, 4-OCH_3, 2-NO_2, 3-NO_2, 4-NO_2, 2-Br, 4-Br, 2-OC_2H_5, 4-OC_2H_5, 2-SCH_3, 4-SCH_3, 4-CO_2H	$\log K_{AgL}/\sigma\ \rho = -0.82$ (H_2O) $\log K_{AgHL}/\sigma\ \rho = -0.68$ (H_2O) $\log K_{AgL_2}/\sigma\ \rho = -0.6$ (H_2O)	307
$Ag^+ + L^- \rightleftharpoons AgL$ L = 4-$RC_6H_4CO_2H$; R = η-C_4H_9, η-C_3H_7, C_2H_5, CH_3, $CH_2{=}CHCH_2$, $CH_2C_6H_5$	$\log K_{AgL}/\sigma^{\star}$	328

ents may make a rational interpretation of a particular correlation very difficult. Under these circumstances, the validity and usefulness of the correlation is questionable.

The principal usefulness of the numerous correlations involving non-equilibrium or non-kinetic data appears to be that of providing support for other experimental data concerned with the elucidation of a particular structural or reactivity pattern. Undoubtedly more correlations of this sort will be observed which will further illustrate the ability of a metal center to absorb and transmit the electronic effect of a substituent or substituents associated with a phenyl ring which is directly or indirectly ligated to the metal center.

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