NMR Study of the Reaction of RuH$_2$(PMe$_3$)$_4$ with Brønsted Acids. (a) Reaction with Phenol in THF-*d*$_8$. An NMR tube containing RuH$_2$(PMe$_3$)$_4$ (47 mg, 0.11 mmol) and phenol (110 mg, 1.1 mmol) was capped with a rubber septum under argon. THF-d_8 (ca. 0.5 mL) was introduced by a syringe. ^{31}P{^{1}H} and ^{1}H NMR spectra of the mixture were measured after keeping it at room temperature for 1 h: ^{31}P{^{1}H} NMR (−60 °C, external 85% H$_3$PO$_4$) −10.3 ppm (A$_2$B$_2$ pattern, $\Delta\nu(P_AP_B)$ = 32 Hz, $J(P_AP_B)$ = 39 Hz); ^{1}H NMR (−40 °C) δ 9.9 (O*H*), 7.3–7.0 (C$_6H_5$), 1.3–1.2 (P(C*H*)$_3$)$_3$, −8.2 (Ru*H*).

(b) Reaction with Phenol in Acetone-*d*$_6$. After RuH$_2$(PMe$_3$)$_4$ (60 mg, 0.15 mmol) and phenol (75 mg, 0.80 mmol) were introduced into an NMR tube equipped with a glass joint, acetone-d_6 (ca. 0.7 mL) was transferred by trap-to-trap distillation. ^{1}H and ^{2}H NMR spectra were measured soon after sealing the sample tube: ^{1}H NMR (−40 °C) δ 12.4 (O*H*), 7.2–6.8 (C$_6H_5$), 1.5–1.3 (P(CH_3)$_3$), −7.9 (Ru*H*); ^{2}H NMR (−70 °C) 10.5 ppm (O*D*). The ^{1}H NMR spectrum after reaction at room temperature for 13 min showed the decrease of peak area of OH and RuH hydrogen signals to ca. 40% of the initial peak areas. These signals disappeared completely after reaction at room temperature for 26 min, although the ^{31}P{^{1}H} NMR spectrum showed retention of the same spectroscopic pattern as for 4.

(c) Reaction with 1,1,1,3,3,3-Hexafluoro-2-propanol in Acetone-*d*$_6$. After RuH$_2$(PMe$_3$)$_4$ (66 mg, 0.16 mmol) and 1,1,1,3,3,3-hexafluoro-2-propanol (140 mg, 0.83 mmol) were introduced into an NMR tube equipped with a glass joint, acetone-d_6 (ca. 0.8 mL) was transferred by trap-to-trap distillation. ^{31}P{^{1}H} and ^{1}H NMR spectra of the reaction mixture were measured soon after sealing the sample tube: ^{31}P{^{1}H} NMR (−40 °C, external H$_3$PO$_4$) −9.7 ppm (A$_2$B$_2$ pattern); ^{1}H NMR (−40 °C) δ 9.5 (O*H*), 4.7 (C*H*, septet, *J*(HF) = 7 Hz), 1.5–1.4 (P(CH_3)$_3$), −7.9 (Ru*H*). The ^{31}P{^{1}H} NMR spectrum after reaction at room temperature for 40 min indicated the decrease of the signal at −9.7 ppm to ca. 75% of the initial peak area. The growth of new signals at 21.0, −4.8, and −17.0 ppm (A$_2$MX pattern) was observed. After 80 min the signal at −9.7 ppm decreased to ca. 45%. After 24 h all these signals disappeared to give signals of uncharacterized complexes. The isolation of *cis*-RuH(OCH(CF$_3$)$_2$)(PMe$_3$)$_4$ from the reaction mixture as well as its full characterization by NMR spectroscopy was not feasible due to its instability.

(d) Reaction with HBF$_4$ in Acetone-*d*$_6$. An NMR tube containing RuH$_2$(PMe$_3$)$_4$ (35 mg, 0.085 mmol) and HBF$_4$ (48% aqueous solution, 31 mg, 0.17 mmol) was capped with a rubber septum under argon. Acetone-d_6 (ca. 0.7 mL) was introduced by a syringe. ^{31}P{^{1}H} and ^{1}H NMR spectra of the reaction mixture were measured soon after the preparation of the sample: ^{31}P{^{1}H} NMR (−40 °C, external H$_3$PO$_4$) −8.8 ppm (A$_2$B$_2$ pattern); ^{1}H NMR (−40 °C) δ 11.7 (*H*BF$_4$ and H_2O), 1.5–1.4 (P(CH_3)$_3$), −7.9 (Ru*H*). The ^{31}P{^{1}H} NMR spectrum after reaction at room temperature for 4 h showed partial decomposition of the above signals (to ca. 50%) and the formation of uncharacterized complexes.

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Supplementary Material Available: Figures giving the structures of two independent molecules in the crystals and tables of positional parameters of the hydrogen atoms, anisotropic thermal parameters, and bond distances and angles (10 pages); a table of calculated and observed structure factors (31 pages). Ordering information is given on any current masthead page.

Specific Solvatochromism of the Prototypical Olefin Complexes (η^2-TCNE)M(CO)$_5$ (M = Cr, W) Resulting from n and π Donation of Aprotic Solvents toward the π-Acceptor Ligand

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The solvatochromism of the well-separated long-wavelength charge-transfer bands of the title complexes was studied in 36 aprotic solvents and in dichloromethane solutions of durene and hexamethylbenzene. The observed effects cannot be described with one of the conventional solvent parameters that have been successfully used for other transition-metal carbonyl complexes; however, they may be interpreted consistently in terms of strong n- *and* π-donor contributions from the solvents. Within a three-component M–A–D approximation, the π-accepting TCNE (A) interacts strongly with the low-valent metal fragment (M) on one side and weakly with donor solvents (D) on the other side of the molecular plane. A solvent parameter $E_{CT}(\pi)$ is derived, which should describe the (n + π) donor capability of solvents toward an approximately planar π-electron-accepting entity. The differences between the Cr and W series reflect the dipolar contributions to the total solvent effect.

Introduction

The long-known phenomenon of solvatochromism, i.e. the solvent dependence of absorption features and especially of the color of certain compounds,[1,2] has attracted renewed attention recently because of increasing attempts to understand and design electronic structures of potentially light-harvesting and photosensitizing complexes (excited-state tuning).[3] There is also a more general need for reliable solvent parameters that can be correlated with a number of physical properties and with chemical reactivities of the dissolved species.[1,4] Many of the estab-

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lished solvent scales are based on the solvatochromism of suitable compounds;[1] well-known examples include Reichardt's E_T scale, which is derived from an organic betaine dye molecule,[5] Kosower's Z scale, which is based on an intermolecular charge-transfer (CT) transition of a pyridinium salt,[6] the π^* parameters of Kamlet, Taft, et al., which come from $\pi \rightarrow \pi^*$ transitions of certain nitro aromatics,[7] and the E^*_{MLCT} scale derived by Manuta and Lees from the metal-to-ligand charge-transfer (MLCT) absorption of (2,2-bipyridine)tetracarbonyltungsten(0).[8]

The last scale has meanwhile been used frequently and successfully by us[9] and others[10,11] to describe quantitatively the extent of solvatochromism in numerous complexes where the metal is σ-bonded to coordinating n-donor atoms such as N,[8-10] S,[11a] and P[11b] of the π-acceptor or π-donor ligand. Such an approach works particularly well if protic solvents capable of hydrogen bonding are excluded;[12] also, solvents with more polarizable second-row elements such as chlorinated hydrocarbons or carbon disulfide presented some problems for solvent parametrization.[9,12] Although there are still open questions with respect to the rationalization of the observed effects, especially in systems without a permanent dipole moment,[9b,c,12-14] the E^*_{MLCT} parameters usually work well to describe the solvent dependence of CT transitions.

Organometallic complexes with π type coordination[15] between the metal center and the chromophoric ligand have not been extensively studied in this respect,[16] although such (solvated) species are certainly involved in many important homogeneously catalytic processes.[15,17] Most of the more stable π-bonded olefin complexes do not show conspicuous color changes in different solvents because they absorb at rather short wavelengths;[16] furthermore, the ligand-field transitions often occur at lower energies than the charge-transfer transitions.[16,17] With the extremely strong π-acceptor ligand tetracyanoethylene (TCNE), considerable metal-to-ligand electron exchange often occurs in the ground state of π-bonded complexes, e.g. of platinum metal fragments, so that there too is only a small amount of absorption in the visible region and apparently little solvatochromism of absorption bands.[18]

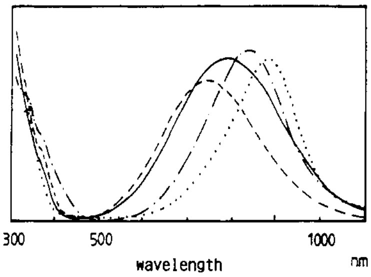

Figure 1. Absorption spectra of (TCNE)Cr(CO)$_5$ in acetonitrile (—), THF (---), benzene (–•–), and cyclohexane (•••). Absorbance scales are different for each spectrum.

We have recently confirmed[19-21] that the deeply colored complexes of TCNE with the prototypical organometallic fragments Cr(CO)$_5$ and W(CO)$_5$ are complexes with a π-coordinated olefin ligand.[20] The single intense (ϵ = 7000 M^{-1} cm^{-1}) charge-transfer absorption band in the long-wavelength region,[19b] the infrared[19] and resonance Raman[21] vibrational data, and the electrochemical characteristics[19] of these complexes could be interpreted within the concept of typical olefin–metal bonding;[22] all evidence points to a molecular orbital situation where the MLCT formulation is only partially valid because of strong metal–ligand mixing in the ground and lowest excited states.[19b] Nevertheless, the reversible reduction of these complexes at potentials close (W system) or even identical with that of the free acceptor ligand TCNE (Cr derivative)[19a] indicates (i) that the metal-to-ligand back-donation comes close to compensating for the olefin-to-metal π-donor interaction and (ii) that the complexes are still strong acceptor systems just as free TCNE itself.[19a]

In our previous report we have presented first evidence that the solvent dependence of the long-wavelength absorption maxima could not be correlated[19b,20b] with existing solvent parameters[1] such as E_T, E^*_{MLCT}, or the D_π scale, which is based on rates of reaction between diphenyldiazomethane and TCNE.[23] Using 36 aprotic solvents, we describe and discuss solvatochromism which differs *qualitatively* from that of all other transition-metal carbonyl compounds. From the ordering of the absorption maxima the empirical solvent parameter $E_{CT}(\pi)$ can be derived.

Experimental Section

Syntheses and characterization of the complexes (TCNE)M(CO)$_5$ (M = Cr, W) have been described previously.[19,20] The best preparative results were obtained when THF *with* the stabilizing inhibitor 2,6-di-*tert*-butyl-4-methylphenol was used for the photogeneration of the intermediate, the solvate (THF)M(CO)$_5$.

Common solvents for absorption measurements were purchased from Aldrich Co. and were of spectrograde quality, if available. The few special, uncommon solvents were used as supplied by the same source. Ethers gave slightly lower absorption maxima of the dissolved complexes if freshly distilled from potassium metal.

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Table I. Charge-Transfer Absorption Maxima $\tilde{\nu}_{max}$ (cm^{-1}) of the Complexes (TCNE)M(CO)$_5$ (M = Cr, W) in Different Solvents (Selected Bandwidths at Half-Height in Parentheses)

solvent	abs max	
	(TCNE)Cr(CO)$_5$	(TCNE)W(CO)$_5$
chloroform	11 100	12 360
carbon disulfide	11 120	12 210[a] 10 050[b]
dichloromethane	11 200 (3000)	12 450 (3000)
trichloroethene	11 280	12 400
1,2-dichloroethane (DCE)	11 320	12 550
tetrachloroethene	11 370	12 400
1,2-dichlorobenzene	11 370	12 450
tetrachloromethane	11 380	12 450[a] 10 300[b]
hexafluorobenzene	11 390	12 640
cyclohexane	11 400	12 400[a] (2600) 10 190[b]
chlorobenzene	11 480	12 700
pentane	11 550 (2500)	12 560[a] (2400) 10 300[b]
cis-cyclooctene	11 610	12 700
nitrobenzene (NB)	11 850	13 300
benzene (BZ)	12 000	13 150
benzonitrile (BN)	12 040	13 470
anisole	12 090	13 130
toluene (Tol)	12 100 (3250)	13 400 (3150)
1-methylnaphthalene	12 280	13 380
diethyl ether	12 640	13 700
1,4-dioxane	12 640	13 800
mesitylene (Mes)	12 670	13 850
acetonitrile (AN)	12 700	14 100[a]
ethyl acetate	13 350	14 450
tetrahydrofuran (THF)[c]	13 490[d] (5300)	14 680 (4900)
cyclohexanone	13 490	14 810
acetone (AC)	13 500 (5300)	14 950 (5500)
1,2-dimethoxyethane (DME)	14 360[e]	15 360

[a] Principal maximum. [b] Shoulder. [c] Contains the stabilizer 2,6-di-*tert*-butyl-4-methylphenol. [d] 13 090 cm^{-1} in freshly distilled THF. [e] 14 080 cm^{-1} in freshly distilled DME.

Absorption measurements were routinely performed with a Shimadzu UV 160 spectrometer. Checks on the Bruins Instruments Omega 10 precision spectrometer showed the values to be correct with an error margin of ±4 nm, corresponding to about ±60 cm^{-1} uncertainty in the wavenumbers.

Results

Figure 1 shows the typical solvatochromic response of the chromium complex. This system displays only one unperturbed absorption band, even in the least polar solvents, while the tungsten analogue exhibits some shoulders in such media.[19b] There are three transitions possible from the three filled d orbitals of the d^6 metal; overlap-forbidden transitions of different polarization and d orbital splitting are likely to be more pronounced in the case of the heavier tungsten system.[10c,24] The band widths at half-height vary between 2400 cm^{-1} (in "nonpolar" solvents) and almost 6000 cm^{-1} (in more "polar" media) and are thus typical for CT transitions.[2]

Table II. Solvatochromism[a] of the Complexes (TCNE)M(CO)$_5$ (M = Cr, W) in Aromatic Solvents and in Tetramethylethene

solvent	abs max	
	M = W	M = Cr
1,2-dichlorobenzene	12 450	11 370
hexafluorobenzene	12 640	11 390
chlorobenzene	12 700	11 480
anisole	13 130	12 090
benzene	13 150	12 000
nitrobenzene	13 300	11 850
tetramethylethene	13 300	12 170
1-methylnaphthalene	13 380	12 280
ethylbenzene	13 390	12 240
toluene	13 400	12 100
benzonitrile	13 470	12 040
1,2-diethylbenzene	13 480	*b*
1,3-diethylbenzene	13 570	*b*
1,4-xylene	13 640	12 300
1,4-diethylbenzene	13 640	*b*
1,3,5-triethylbenzene	13 660	12 500
mesitylene	13 850	12 670
1,2,3,4-tetramethylbenzene	13 910	12 900
durene in CH_2Cl_2[c]	13 350	11 720
hexamethylbenzene in CH_2Cl_2[c]	12 970	11 220

[a] Absorption maxima in cm^{-1}, in the order of hypsochromic shift of the tungsten complex. [b] Rapid decomposition. [c] Saturated solution.

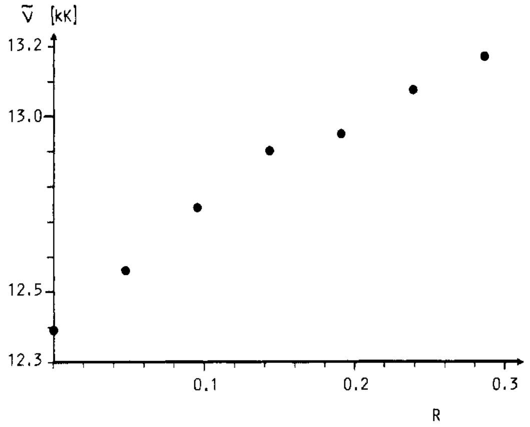

Figure 2. Energy at the absorption maximum (1 kK = 1000 cm^{-1}) of (TCNE)W(CO)$_5$ depending on the molar ratio *R* between durene and dichloromethane.

The complexes are fairly soluble in less coordinating solvents such as (halogenated) hydrocarbons, nitriles, esters, ketones, or ethers; on the other hand, amines and protic solvents cause rapid dissociation, particularly of the chromium complex. Table I summarizes the energies at the absorption maxima measured in 27 more common solvents, listed according to increasing hypsochromic shift for the chromium complex. Table II contains data obtained in seven more alkyl aromatic solvents and in tetramethylethylene; also included are values measured in saturated solutions of hexamethylbenzene and durene (1,2,4,5-tetramethylbenzene) in dichloromethane. The response of the latter system to a changing molar ratio of the medium is depicted in Figure 2. Only the data from Table I were used to derive the new solvent parameter $E_{CT}(\pi)$ (cf. Table IV). Absorption spectra in KBr pellets and diffuse-reflectance spectra of the solid complexes on filter paper showed rather broad bands with maxima around 14000 cm^{-1} in both cases.[21]

Discussion

Solvatochromism occurs if the solvent stabilization of a system is different in the ground and excited states.[1] Strong effects are expected if the transition moment lies antiparallel to the ground-state dipole moment $M^{\delta-} \leftarrow L^{\delta+}$ as in a metal-to-ligand charge-transfer situation.[9,25] The excitation responsible for the long-wavelength bands in the

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Table III. Correlation Coefficients between Solvent Parameters and Data from Table I

param (ref)	no. of data points[a]	*r*: (TCNE)Cr(CO)$_5$	*r*: (TCNE)-W(CO)$_5$
E^*_{MLCT} (9)	17	0.486	0.563
E_T (1, 5)	24	0.260	0.366
π^* (7)	12	0.208	0.556
DN (1, 26)	12	0.908	0.889
D_π (23)	15	0.834	0.807

[a] Solvent parameters were not always available for the solvents used in Table I.

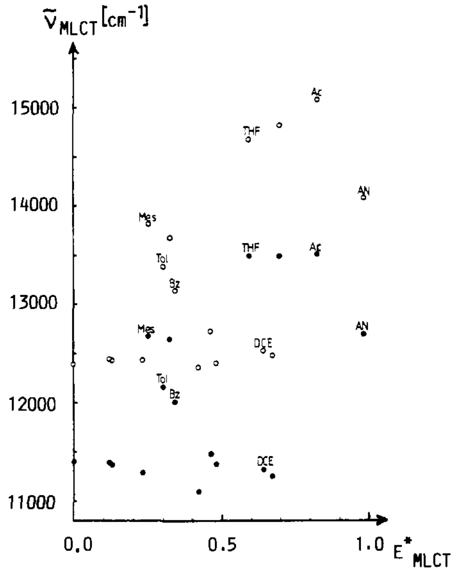

Figure 3. "Correlation" between wavenumbers at the absorption maxima of (TCNE)Cr(CO)$_5$ (●) and (TCNE)W(CO)$_5$ (○) in typical solvents and the solvent parameters E^*_{MLCT}.

complexes (TCNE)M(CO)$_5$ have such charge-transfer character; electrochemical, ESR, and resonance Raman data suggest an uptake of negative charge predominantly by the TCNE ligand in this first excited state.[19,21] The "negative" solvatochromism of (TCNE)M(CO)$_5$ results from the more frequent situation that the metal–ligand bond polarity is reduced by charge transfer in the excited state.[9c] Similarly, the width of the bands and the extent of solvatochromism, covering absorption maxima differences of about 3200 cm^{-1} (ca. 0.4 eV) as one goes from chloroform to the certainly not too "polar" 1,2-dimethoxyethane, are quite in agreement with what one would expect for the CT transition of a carbonyl complex.[2,8-14]

However, there is virtually no correlation of the energies at the absorption maxima with the well-established solvent parameters E^*_{MLCT},[8] E_T,[5] and π^*,[7] as indicated by the poor correlation coefficients in Table III and by the scatter displayed in Figure 3. The overall correlation is a little better with the donor numbers (DN)[26] of Gutmann or the D_π values of Nagai, Oshima, et al.;[23] still, the correlation coefficients $r < 0.91$ are far from being satisfactory. DN parameters were derived from enthalpy measurements of Lewis σ-donor/σ-acceptor complexes with SbCl$_5$ as σ acceptor;[1,26] the D_π values were obtained from kinetic studies of the diphenyldiazomethane addition to TCNE.[23]

The failure of existing solvent "polarity" scales to correlate with the measured absorption maxima of the complexes (TCNE)M(CO)$_5$ prompted us to derive an empirical solvent parameter. Arbitrarily assigning the values S(Cr,W) = 0.0 (1.0) to those solvents (chloroform and 1,2-dimethoxyethane, respectively) in which the lowest (highest) transition energies were observed, we arrived by linear interpolation at the numbers *S* compiled in Table IV. Average values [*S*(Cr) + *S*(W)]/2 = $E_{\mathrm{CT}}(\pi)$ were used as new solvent parameters; those cases with relatively large differences between the chromium and tungsten systems will be discussed below.

Table IV. Solvent Parameters $E_{\mathrm{CT}}(\pi)$ as Defined from Solvatochromism of π Complexes (TCNE)M(CO)$_5$ (M = Cr, W)

solvent	*S*: M = Cr	*S*: M = W	$\bar{S}$ = $\mathrm{E}_{\mathrm{CT}}(\pi)$[b,c]	ΔS = *S*(W) - *S*(Cr)
carbon disulfide	0.0061	−0.0500	−0.044	−0.0561
chloroform	0.0000[a]	0.0000[a]	0.000[a]	0.0000
dichloromethane	0.0307	0.0300	0.030	−0.0007
trichloroethene	0.0552	0.0133	0.034	−0.0419
tetrachloroethene	0.0828	0.0133	0.048	−0.0695
cyclohexane	0.0920	0.0133	0.053	−0.0787
1,2-dichlorobenzene	0.0828	0.0300	0.056	−0.0528
tetrachloromethane	0.0859	0.0300	0.058	−0.0559
1,2-dichloroethane (DCE)	0.0675	0.0633	0.065	−0.0042
hexafluorobenzene	0.0890	0.0933	0.091	+0.0043
pentane	0.1380	0.0667	0.102	−0.0713
chlorobenzene	0.1165	0.1133	0.115	−0.0032
cis-cyclooctene	0.1609	0.1133	0.137	−0.0476
benzene (BZ)	0.2761	0.2633	0.270	−0.0128
nitrobenzene (NB)	0.2301	0.3133	0.272	+0.0832
anisole	0.3037	0.2567	0.280	−0.0470
toluene (Tol)	0.3067	0.3467	0.327	+0.0400
benzonitrile (BN)	0.2883	0.3700	0.329	+0.0817
1-methylnaphthalene	0.3619	0.3400	0.351	−0.0219
diethyl ether	0.4724	0.4467	0.455	−0.0257
1,4-dioxane	0.4724	0.4800	0.476	+0.0076
mesitylene (Mes)	0.4816	0.4967	0.489	+0.0151
acetonitrile (AN)	0.4908	0.5800	0.535	+0.0892
ethyl acetate	0.6902	0.6967	0.694	+0.0065
tetrahydrofuran (THF)	0.7331	0.7733	0.753	+0.0402
cyclohexanone	0.7331	0.8167	0.775	+0.0836
acetone (AC)	0.7362	0.8633	0.800	+0.1271
1,2-dimethoxyethane (DME)	1.0000[a]	1.0000[a]	1.000[a]	0.0000

[a] By definition. [b] (TCNE)Cr(CO)$_5$: E_{MLCT} (cm^{-1}) = 3260 cm^{-1} × $E_{\mathrm{CT}}(\pi)$ + 11 100 cm^{-1}; $r = 0.996$. [c] (TCNE)W(CO)$_5$: E_{MLCT} (cm^{-1}) = 3000 cm^{-1} × $E_{\mathrm{CT}}(\pi)$ + 12 360 cm^{-1}; $r = 0.997$.

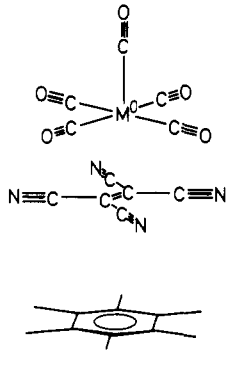

Figure 4. Idealized structural arrangement for the π interaction of one aromatic solvent molecule with the olefin complex (TCNE)M(CO)$_5$.

We interpret the failure of existing solvent parameters to describe the solvatochromism of complexes (TCNE)M(CO)$_5$ to a rather specific solvent–solute interaction. With the assumption of an idealized geometry[22c] of the pentacarbonylmetal olefin complex as shown in Figure 4, the complexes display an open side of still very π-electron-deficient TCNE for specific solvent coordination. The

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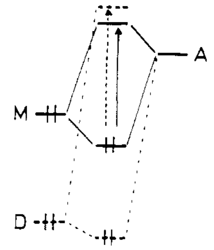


Figure 5. MO energy diagram illustrating the effect of specific solvent donor (D) contribution (- - -) to a typical MLCT situation (—) (filled metal d orbital M and empty ligand acceptor orbital A). A small additional orbital splitting due to a weak D–A interaction destabilizes particularly the acceptor orbital and thus causes an increase of the M → A transition energy.

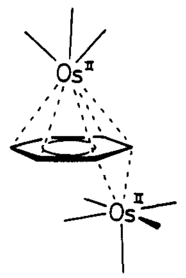
relevant interaction would then be the combined n and π donation[27a] from the solvent to the π-accepting TCNE in the complex; the following examples illustrate that such an interpretation helps to account for the major "unconventional" solvent effects observed.

Most revealing is certainly the series of aromatic compounds listed in Table II. It is obvious that—in contrast to conventional "polarity" ordering—the higher alkyl substituted aromatic solvents cause the larger hypsochromic shifts, whereas the very polar nitrobenzene with its large dielectric constant and molecular dipole moment has virtually the same solvent effect as benzene itself! Halogenated aromatic solvents cause a slight bathochromic shift relative to benzene. There is a rough correlation between the ionization potential of the aromatic compounds[27b] and their solvent effect toward (TCNE)M(CO)$_5$; however, there are some ambidentate n and π donors such as anisole, nitrobenzene, and benzonitrile where the electron pair (n) donating functional group may be able to interfere with the coordination to the aromatic π system of the solvent.[27a] Nevertheless, these results point to a *competition* of the π-electron-rich organometallic fragment M(CO)$_5$ (M) with the donor solvent (D) for the planar acceptor TCNE (A): The stronger the solvent donor, i.e. the more pronounced the A–D interaction, the weaker the M–A interaction *within* the complex (TCNE)M(CO)$_5$ and the higher the hyposochromic shift. The solvent thus moderates the TCNE acceptor effect toward the electron-rich organometal center via n or π type donor interactions. The molecular orbital diagram in Figure 5 describes such an unsymmetrical three-component M–A–D interaction.

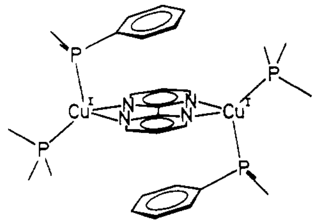
An experiment using different ratios of π-electron-donating durene (mp 82 °C) relative to dichloromethane (Figure 2) shows the expected nonlinear behavior for $\tilde{\nu}_{CT}$; however, it also illustrates that the D → (A–M) interaction is not that large in order to shift the equilibrium (1) very far to the right side: The illustration in Figure 4 is just a momentary view of how one aromatic solvent molecule can maximally affect the binary complex and does not represent (yet) the *inert* ternary complex M–A–D.

$$\text{(TCNE)M(CO)}_5\cdot n\text{CH}_2\text{Cl}_2 + \text{durene} \rightarrow \text{(TCNE)M(CO)}_5\cdot\text{durene} + n\text{CH}_2\text{Cl}_2 \quad (1)$$

The capability of planar π-acceptor ligands to function as bifacially coordinating centers in an *inverse sandwich complex* situation has recently been demonstrated for the M–A–M system 1 with η^2:η^6-C$_6$H$_6$ as A and Os(II) ammine fragments as M;[28a] a D–A–D situation involving two phosphane phenyl rings as donors and coordinated 2,2′-bipyrimidine as the central acceptor (2) was structurally characterized.[28b]

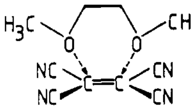


1



2

Other "unusual" solvent effects include the stronger response of less polar ketones in comparison to the effect of more polar nitriles; the former are better π donors than the latter, as shown recently by Taube and co-workers, who prepared e.g. pentammineosmium(II) complexes of acetone.[29] Ethers must be viewed as n donors via their oxygen lone pairs; however, Oshima et al. have already suggested[23a] that bifunctional DME (diglyme) may interact particularly strongly with a planar π-acceptor system through an "organic chelate effect", as shown in 3. In fact, DME is the solvent in which the complexes (TCNE)M(CO)$_5$ show by far the most pronounced hypsochromic shift *without* rapid decomposition.



3

It is interesting to note from Table IV that aliphatic hydrocarbon solvents display a weak donor effect (from C–H or C–C σ bonds?)[30a] when compared to related chlorinated hydrocarbons.[30b] This phenomenon is more pronounced for the tungsten complex than for the chromium analogue, and the variation of differences $\Delta S = S(\mathrm{W}) - S(\mathrm{Cr})$ deserves some comment. We have noted previously that the tungsten system displays more pronounced MLCT character than the chromium analogue; olefin π electron donation and π back-bonding compensate each other to a larger extent in (TCNE)Cr(CO)$_5$, resulting in a more delocalized TCNE–metal bonding.[19,21] This means that the dipole contributions should be smaller for the chromium complex than for the tungsten system, an

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[27] (a) A reviewer suggested two-dimensional fitting[27c] with parameters related to n and π donation. In view of the dangers of multiparameter approaches we do not consider the available data base sufficient to draw detailed conclusions from such a treatment. (b) Cf.: Bock, H.; Kaim, W. *Chem. Ber.* **1978**, *111*, 3552 and literature cited therein. (c) Buncel, E.; Rajagopal, S. *Acc. Chem. Res.* **1990**, *23*, 226.

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assumption that is fully supported by the observed differences ΔS (Table IV). Large deviations ΔS result in those solvents that are highly dipolar themselves such as ketones, nitriles, and nitrobenzene; therefore, the more dipolar tungsten complex is more strongly stabilized in the ground state, and a more pronounced hypsochromic shift is the result. On the other side, the most negative differences ΔS are observed in the aliphatic hydrocarbon solvents pentane and cyclohexane; these solvents are not dipolar, nor do they contain polarizable second-row-element heteroatoms such as Cl or S.

In summary, the unusual electronic structures and absorption spectra of the (olefin)carbonylmetal complexes (TCNE)M(CO)$_5$ have allowed us to quantify a specific solvatochromism that is based on the n- *and* π-donor capability of the medium toward an approximately[21,22c] planar π-acceptor system. The empirical parameters $E_{\mathrm{CT}}(\pi)$ for aprotic solvents derived from this study may be of value for other π-electron-accepting organometallic compounds with planar ligand "decks" such as (η^6-arene)$_2$Fe^{2+}[31] or for electron-poor square-planar complexes with d^8 metal centers. Another area of potential application is the electron-transfer reactivity of aromatics where (radical) ion-pair complexes with planar, coordinatively unsaturated π acceptors can occur as intermediates.[32]

Acknowledgment. Generous support for this work has come from the Deutsche Forschungsgemeinschaft and Volkswagenstiftung.

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Stabilization of Iridium(I), -(III), and -(V) in an Oxygen-Donor Ligand Environment and the Selective Dehydrogenative Silylation and Hydrosilylation of Ethylene with {C(Ph$_2$P=O)$_3$}Ir(ol)$_2$

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Ir(I), -(III), and -(V) can be stabilized in an O-donor ligand environment, as shown by the preparation of (triso)Ir(ol)$_2$ (**1**; triso = tris(diphenyloxophosphoranyl)methanide; ol = C$_2$H$_4$ (**a**), cyclooctene (coe) (**b**)), (triso)Ir(SiPh$_3$)H(C$_2$H$_4$) (**2**), and (triso)Ir(H)$_2$(SiPh$_2$Me)$_2$ (**3a**). **1a**,**b** are selective catalysts for the dehydrogenative silylation and hydrosilylation of ethylene with triphenylsilane and diphenylmethylsilane. Complex **2** is a rare example of an alkene silyl hydride and is a proposed catalytic intermediate.

Introduction

Interest in how the properties of organometallic compounds change on moving from the more common P- and C-donor sets to an O-donor set has increased in recent years.[1] Studies by Yermakov, Schwartz, and others[2] of site-isolated organometallic fragments supported on oxide surfaces show that an O-donor ligand environment leads to species with interesting catalytic properties. The cobalt ligand[3] [CpCo(R$_2$PO)$_3$]$^-$, the trisilanol[4] [(Cy)$_7$Si$_7$O$_{12}$H$_2$], and the triphosphate[5] [P$_3$O$_9$]$^{3-}$ are tridentate O-ligands that can form rare examples of stable organometallic complexes. We felt that O-donor ligands[6] might provide for chemically robust catalysts, particularly for alkane conversion.

We show that the triso ligand (triso = tris(diphenyloxophosphoranyl)methanide) prepared by Grim et al.[7] binds to Ir(I), -(III), and -(V). Compounds of Ir(I) and Ir(III) are relatively common, but examples of Ir(V) are very rare, being limited to phosphine and cyclopentadienyl polyhydrides and related compounds. We also demonstrate that (triso)Ir(ol)$_2$ (**1**; ol = C$_2$H$_4$ (**a**); coe (**b**)) are the first homogeneous O-donor catalysts for the dehydrogenative silylation and hydrosilylation of ethylene. Some of this work has been reported in a communication.[6b]

Stoichiometric Reactions with Silanes

We recently reported the preparation of the O-donor alkene complex (triso)Ir(C$_2$H$_4$)$_2$ (**1a**), which is formed in

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