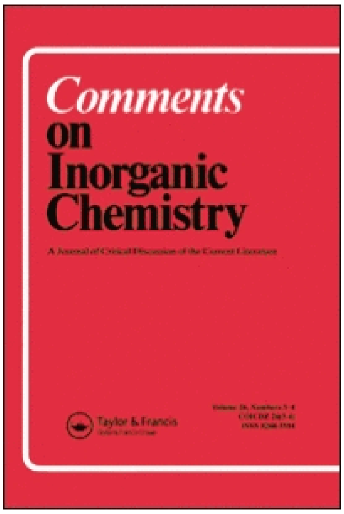

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Arene Displacement Reactions of (η^6-Arene)chromium(0) Carbonyl Compounds

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Arene Displacement Reactions of (η^6-Arene)chromium(0) Carbonyl Compounds

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INTRODUCTION

The development of organometallic chemistry over the past 25 years has led to extremely selective catalytic systems and to a greater understanding of their mechanisms. One area of particular interest has been the study of hydrogenation reactions (e.g., dienes to monoenes) using (η^6-arene)tricarbonylchromium(0) complexes as catalysts.[1–4] The possibility of the catalytic liberation of functionalized arenes from the chromium centers in such compounds has also attracted the attention of synthetic organic chemists.[5,6]

The mechanisms involved in catalytic hydrogenation by (η^6-arene)tricarbonylchromium compounds are only just becoming understood despite the fact that these reactions have been investigated since the early sixties. The first step is believed to be partial (or complete) displacement of the arene ring from the chromium

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metal center.[1-7] Moreover, the catalytic rate is highly dependent on the nature of the arene involved, i.e., on the strength of the arene–Cr bond.[2] In this Comment, the work that has been reported on arene displacement reactions of (η^6-arene)chromium(0) carbonyl compounds is discussed together with its relevance to the mechanism of catalytic hydrogenation.

ARENE EXCHANGE IN (η^6-ARENE)TRICARBONYL CHROMIUM(0) COMPLEXES

Activation of arene–chromium bonds was first noted when arene exchange in (η^6-arene)$Cr(CO)_3$ was observed in various arene solutions (Eq. (1))[8,9]:

$$(Ar)Cr(CO)_3 + Ar' \rightarrow (Ar')Cr(CO)_3 + Ar \qquad (1)$$

The displacement of one arene (Ar) by another (Ar') takes place in the following order, going from the most to the least reactive *arene:*

$C_6Me_6 > C_6H_2Me_4 > C_6H_3Me_3 > PhNMe_2 > C_6H_4Me_2 > PhMe = C_6H_6 > PhCOMe = PhOMe > PhCO_2Me > PhCl = PhF > C_{10}H_8$

The driving force in Eq. (1) is the greater thermodynamic stability of $(Ar')Cr(CO)_3$ relative to $(Ar)Cr(CO)_3$ due to the increased electron-donating capability of Ar'.[10] This situation is reflected in greater ease of displacement with increasing alkyl substitution in Ar'.

The first kinetic studies were reported in 1961 by Strohmeier and co-workers[11] for the exchange of ^{14}C-labelled benzene, toluene, and chlorobenzene (Ar*) with their corresponding unlabelled (η^6-arene)tricarbonylchromium(0) complexes (Eq. (2)):

$$(Ar)Cr(CO)_3 + Ar^* \rightarrow (Ar^*)Cr(CO)_3 + Ar \qquad (2)$$

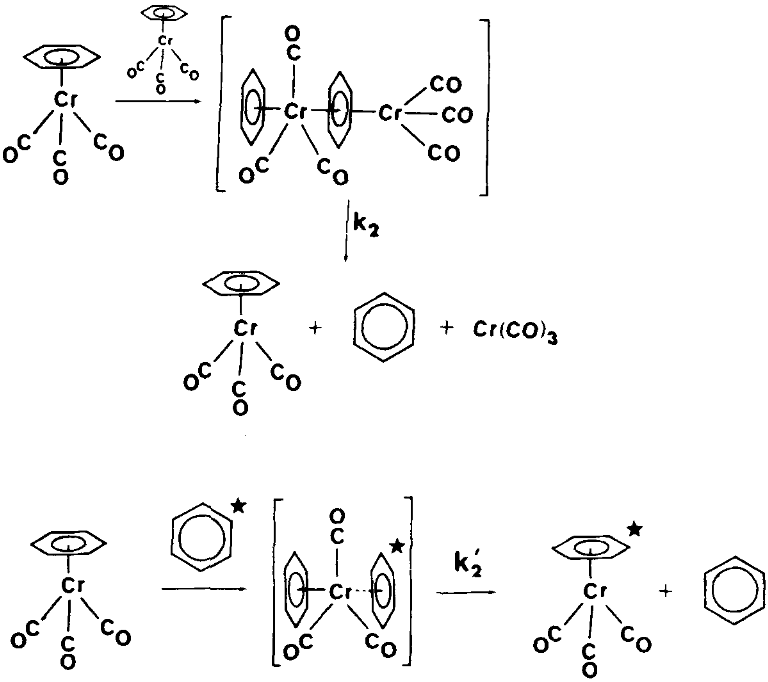
The rate law obtained showed both a first- and second-order dependence on the starting arene complex as well as a first-order dependence on the arene:

$$-d[(\mathrm{Ar})\mathrm{Cr}(\mathrm{CO})_3]/dt$$

$$= k_2[(\mathrm{Ar})\mathrm{Cr}(\mathrm{CO})_3]^2 + k_2'[(\mathrm{Ar})\mathrm{Cr}(\mathrm{CO})_3][(\mathrm{Ar}^*)] \quad (3)$$

Scheme I for arene exchange was proposed. Among the criticisms of this scheme was the fact that it could not account for the acceleration of the reaction rates in the presence of a coordinating ligand,[10,12] nor was the expected inversion observed when the two sides of the arene ring were distinguishable.[13]

SCHEME I



★ = ^{13}C-labelled

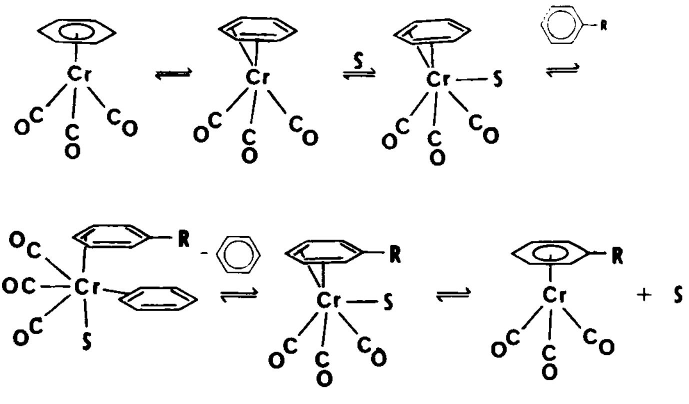
A new mechanism was postulated by Mahaffy and Pauson[10] where a partial displacement of the arene (η^6 to η^4) from the metal was initiated by the coordinating solvents (Scheme II). In the absence of a coordinating solvent, it has recently been proposed that a second molecule of the arene–chromium complex could catalyze the reaction by coordinating through the carbonyl oxygen.[14]

A thorough reinvestigation of the arene exchange reaction by Traylor and his research group[14–17] has given new insight into the rate laws and mechanisms involved in arene exchange. The nature of the second-order dependence on the reactant arene complex in Eq. (3) was questioned. When an inert Cr complex is added, a first-order dependence on the added Cr complex is observed.[14] The true second-order term appears to be

$$k_2[(\mathrm{Ar})\mathrm{Cr(CO)_3}][\{\mathrm{ArCr(CO)_3}\}\{\mathrm{Ar^*Cr(CO)_3}\}] \qquad (4)$$

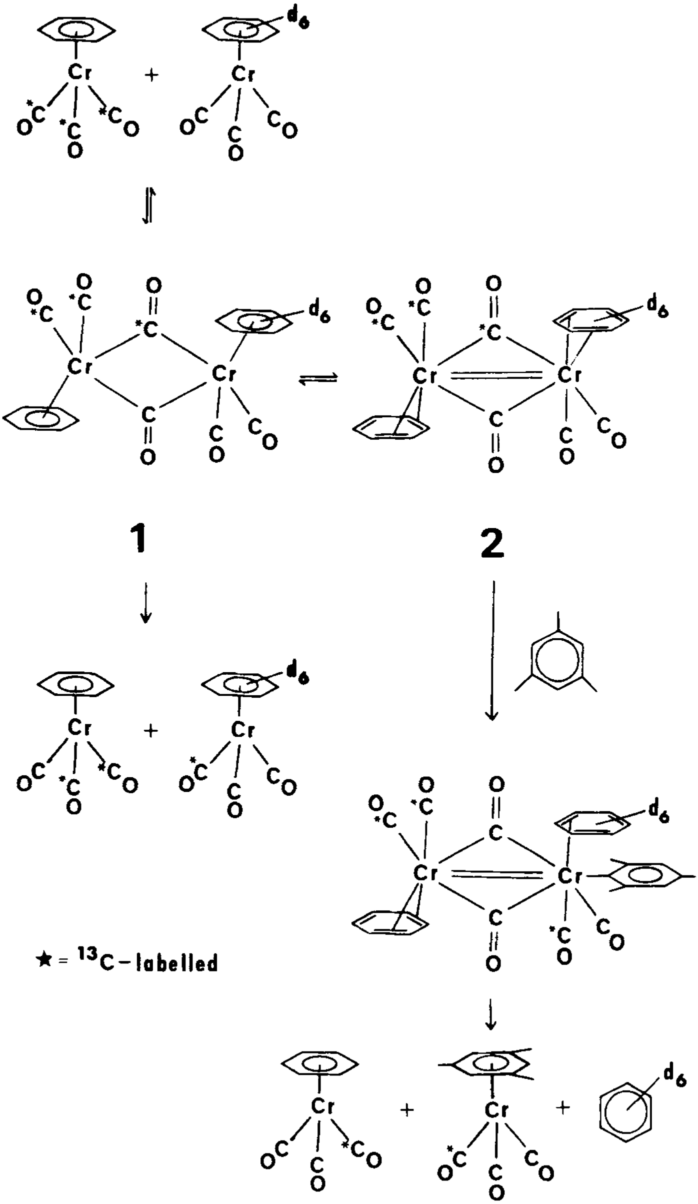
Therefore, in the absence of a coordinating solvent, the reaction is likely to be catalyzed by another arene complex and the intermediate is postulated to be dimeric, possibly bridging in nature.[16]

SCHEME II



S = SOLVENT

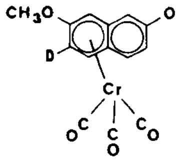
SCHEME III



★ = ^{13}C-labelled

Support for this hypothesis comes from the presence of rapid carbon monoxide scrambling between (η^6-C_6H_6)Cr(^{13}CO)$_3$ and (η^6-C_6Me_6)Cr(^{12}CO)$_3$ even before arene exchange was observed. Scheme III was formulated to explain the presence of internal CO exchange as well as arene exchange.[16] The occurrence of both ^{13}CO and arene exchange can be satisfied by the CO-bridged intermediates 1 and 2. Since arene exchange is now generally believed to proceed by η^4-bonded arenes, intermediate 2 is the more likely candidate. The remaining steps are consistent with Scheme II.

Arene exchange in polycyclic (η^6-arene)tricarbonylchromium(0) complexes is more facile than in monocyclic complexes.[18,19] The catalytic hydrogenation rate of the chromium complexes increases when the arene is phenanthrene, napthalene, or anthracene.[2] In selectively-deuterated napthalene complexes, intramolecular ring exchange occurs at a much faster rate than intermolecular arene exchange with benzene.[18] This "haptotropic rearrangement" clearly indicates the facility of ring slippage in napthalene that provides a free coordination site for an incoming ligand. There is a stereochemical dependence in the haptotropic migrations of methoxy-substituted (η^6-napthalene)tricarbonylchromium(0) complexes since the rate constant for exchange in complex 3 is 14 times greater than in complex 4.[20]



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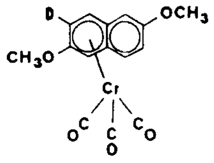
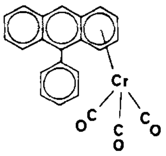


4

Heating the phenylanthracene complex 5 leads to migration of the Cr(CO)$_3$ moiety between two nonadjacent six-membered rings (from 5 to 6).[21] Complex 6 reverts back to 5 when left standing at room temperature overnight.



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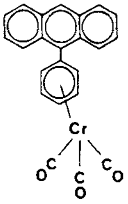
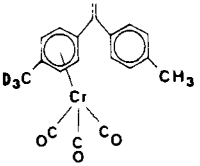


6

Since olefin-catalyzed arene exchange had been shown to occur,[22] Traylor and Stewart also studied the effect of extending the π-system on inter- and intramolecular arene exchange.[17] The effects of the alkene on both internal and external arene exchange in the diphenylethene isomers, 7–9, were analyzed.



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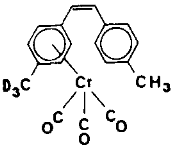

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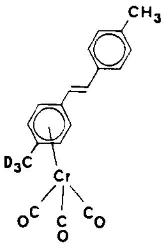


9

The results gave the following order of reactivity for internal arene exchange 7 > 8 > 9, while that for external exchange with benzene was 9 > 7 > 8. The rate of internal exchange was accelerated by the presence of the alkene. Ring slippage could occur by either a two- or a three-step process (Scheme IV). The two-step mechanism would result in a saturated transition state, while the alternative mechanism would give an unsaturated transition state. Because of the distal uncomplexed arene ring, only the two-step mechanism would not be operative for complex 9.

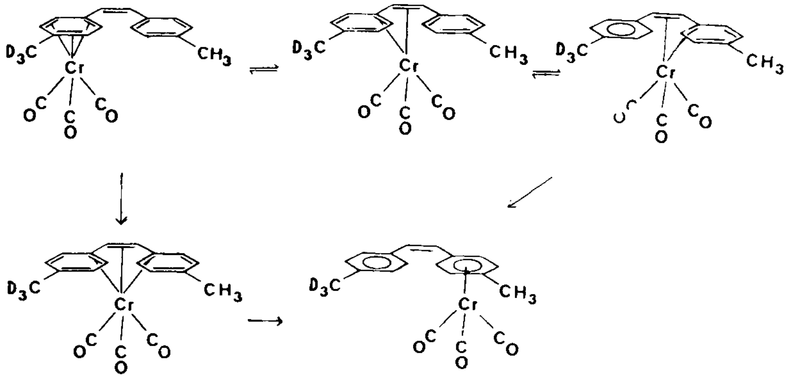
Surprisingly, the effect of a catalyst caused an acceleration in the internal exchange rate of only complex 9, although the external exchange rate of both compounds 8 and 9 increased. The increase in the external exchange could result from the synergistic catalysis of the acetone and internal alkene catalyst. The greater unsaturation of the transition state could also explain the increase in internal exchange for the case of complex 9.

ARENE EXCHANGE REACTIVITY IN (η^6-ARENE)CHROMIUM(0) COMPLEXES

Comparisons of arene exchange have been obtained for cases where one carbonyl group has been substituted by another ligand. Such systems were constructed to facilitate arene exchange and allow for efficient nucleophilic addition.[22] The bonding properties of the substituted ligand were considered when predetermining possible reactivity of the arene ligand.

The replacement of a carbonyl ligand by PPh_3, $AsPh_3$, or $SbPh_3$

SCHEME IV



results in large shifts in ν(CO) to lower wavenumbers.[23] The electron-donating properties of the substituent ligand increase the electron density on the chromium atom, thereby allowing for greater metal–arene back-donation. The displacement of the arene should therefore be more difficult. An anticipated decrease in the catalytic ability of the (η^6-arene)$Cr(CO)_2(PPh_3)$ did occur.[24] An enhancement of arene exchange in (η^6-arene)$Cr(CO)_3$ by replacement of one CO with the diphos ligand ($Ph_2PCH_2CH_2PPh_2$) was postulated.[22] The chelating capability of diphos was expected to possibly stabilize the η^4 intermediate. However, arene exchange occurred at an even slower rate than for the PPh_3 complex. The increase in the strength of the arene–Cr bond overwhelmed any coordinating effect of the bidentate diphos ligand.

The similarity of the thiocarbonyl (CS) ligand to CO made it a logical choice to study.[23] The fact that the CS is a better σ-donor and π-acceptor ligand than CO should accelerate arene exchange by weakening the arene–Cr bond. Unfortunately, this could not be demonstrated, as only decomposition was observed.

LIGAND DISPLACEMENT OF ARENES IN (η^6-ARENE) CHROMIUM(0) CARBONYL COMPLEXES

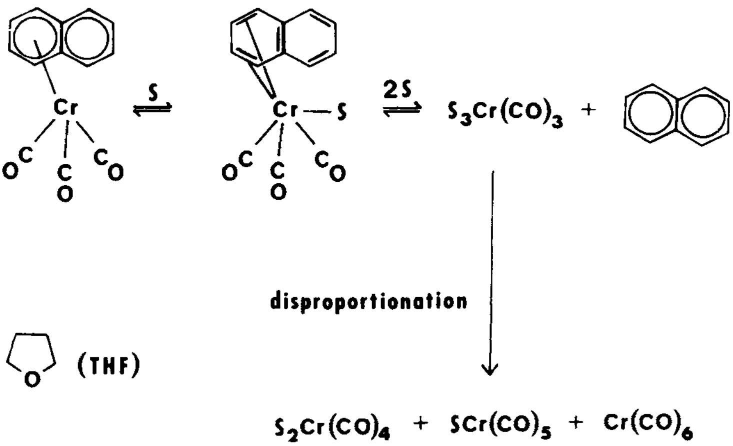
The initial steps involved in arene exchange of the (η^6-arene)-tricarbonylchromium(0) complex in the presence of coordinating solvents (S) have been postulated to be ring slippage and coordination of solvent (Eq. (5)).[2] If free arene was present in the reaction solution, the coordinated solvent should be replaced by

$$(Ar)Cr(CO)_3 + 3S \rightarrow Cr(CO)_3(S)_3 + Ar \qquad (5)$$

the free arene. Tetrahydrofuran solutions of (η^6-napthalene)$Cr(CO)_3$ were left standing at room temperature under nitrogen and were monitored by IR spectroscopy.[23] The appearance of new ν(CO) bands was attributed to intermediates containing one, two, and three molecules of coordinated THF (Scheme V). The study was facilitated by the lability of the napthalene–Cr bond.

The reaction of (η^6-napthalene)$Cr(CO)_3$ with $P(OMe)_3$ in deca-

SCHEME V



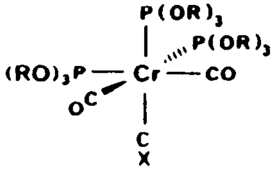
lin yielded *fac*-$Cr(CO)_3[P(OMe)_3]_3$ (Eq. (6)).[19] The rate law showed a second-order dependence on both the Cr complex and $P(OMe)_3$.

$$(\eta^6\text{-napthalene})Cr(CO)_3 + 3P(OMe)_3 \rightarrow fac\text{-}Cr(CO)_3[P(OMe)_3]_3 + \text{napthalene} \qquad (6)$$

The replacement of a carbonyl ligand by a thioether ligand,[25] SR^1R^2, results in complexes of the type $(\eta^6\text{-PhR})Cr(CO)_2(SR^1R^2)$ which have three possible sites for ligand displacement—the arene, carbonyl or thioether ligands. Overnight stirring of the thioether complexes in the presence of a ligand L in a polar solvent at room temperature yields a variety of products. Ligand displacement at all three sites occurs, although preference for formation of the pentacarbonyl species indicates facile loss of the arene and the weakly coordinated thioether ligand.

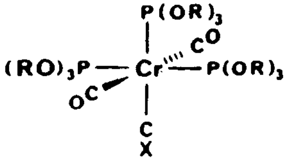
$$(\eta^6\text{-PhMe})Cr(CO)_2(SR^1R^2) + L \xrightarrow{\text{THF}} (\eta^6\text{-PhMe})Cr(CO)_3 + (\eta^6\text{-PhMe})Cr(CO)_2L + Cr(CO)_5L + Cr(CO)_5(SR^1R^2) \qquad (7)$$

The thio- and selenocarbonyl analogues of $(\eta^6\text{-PhCO}_2Me)Cr(CO)_3$ were expected to undergo faster reactions with $P(OMe)_3$ because of their anticipated weaker arene–Cr bonds.[26] The products obtained are a mixture of *fac*- and *mer*-$Cr(CO)_2(CX)[P(OMe)_3]_3$ (X = S, Se) isomers (structures 10–12).



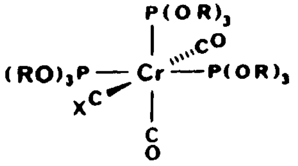
fac

10



mer I

11



mer II

12

R = Me, Et, n-Bu, Ph
X = S, Se

Kinetic studies established a rate expression having a dependence on both the chromium complex and $P(OMe)_3$.[27] The reactivity dependence of the R group on the arene ligand is similar to that for the corresponding tricarbonylchromium complexes. The reaction rate decreases when the number of methyl groups is increased. The increase in the electron-donating ability of the arene ring results in a strengthening of the arene–metal bond. Conversely, the use of electron-withdrawing groups leads to an enhancement of the ring lability. The reactivity for arene displacement by tertiary phosphites decreases in the following order:

$$(n\text{-BuO})_3P > (EtO)_3P > (MeO)_3P > (PhO)_3P > (C_6H_{11}O)_3P$$

Further CO displacement in the thiocarbonyl complex[27] by $P(OPh)_3$ affords (η^6-$PhCO_2Me)Cr(CO)(CS)[P(OPh)_3]$ which is unreactive in the presence of $P(OMe)_3$. This observation could be attributed to an increase in arene–metal bond strength due to the donating $P(OPh)_3$ ligand or possibly to the steric hindrance caused by $P(OPh)_3$.

Of particular interest is the preferred formation of the isomer 11 over 10, which is the sole product in the analogous tricarbonyl case (Eq. (6)). When the reaction of (η^6-$C_6H_6)Cr(CO)_2(CSe)$ with $P(OPh)_3$ was monitored by ^{31}P NMR,[27] greater amounts of *fac*-$Cr(CO)_2(CSe)[P(OPh)_3]_3$ than the *mer-I* isomer were initially produced. However, the final product was the *mer-I* isomer, indicating that the *mer-I* isomer is thermodynamically more stable while the *fac* isomer is kinetically favored. The rearrangement mechanism of the *mer-I* to *mer-II* isomerization has been investigated by the powerful new technique of 2-D NOE ^{31}P NMR spectroscopy.[28] On the basis of the assignments for the ^{31}P resonances of the three $Cr(CO)_2(CX)[P(OMe)_3]_3$ (X = S, Se) isomers, it has been possible to show the 2-D correlations between the *mer-I* and *mer-II* isomers (Fig. 1). The map clearly reveals the exchange occurring between the doublet of the *mer-II* isomer at 191.4 ppm with the doublet and triplet of the *mer-I* isomer at 188.6 and 181.2 ppm, respectively. Examination of arene displacement from (η^6-arene)-$Cr(CO)_3$ (arene = benzene, methyl benzoate, dimethyl aniline) by $P(OMe)_3$ resulted in a mixture of *fac*- and *mer*-$Cr(CO)_3[P(OMe)_3]_3$.[29]

Moreover, from a detailed analysis of the FT-IR spectra of the reaction mixtures, these exchanges and those between the *fac* and *mer* isomers take place intramolecularly.[27] Similar intramolecular exchanges have been reported for several other group 6B metal carbonyl complexes such as $Cr(CO)_4[C(OMe)](PR_3)$ ($R = Et, C_6H_{11}$)[30] and $M(CO)_{6-n}(PR_3)_n$ (M = Cr, Mo, W; R = Me, Et, *n*-Bu, OMe, OEt; n = 1, 2).[31]

The most interesting result of the 2-D experiments is the fact

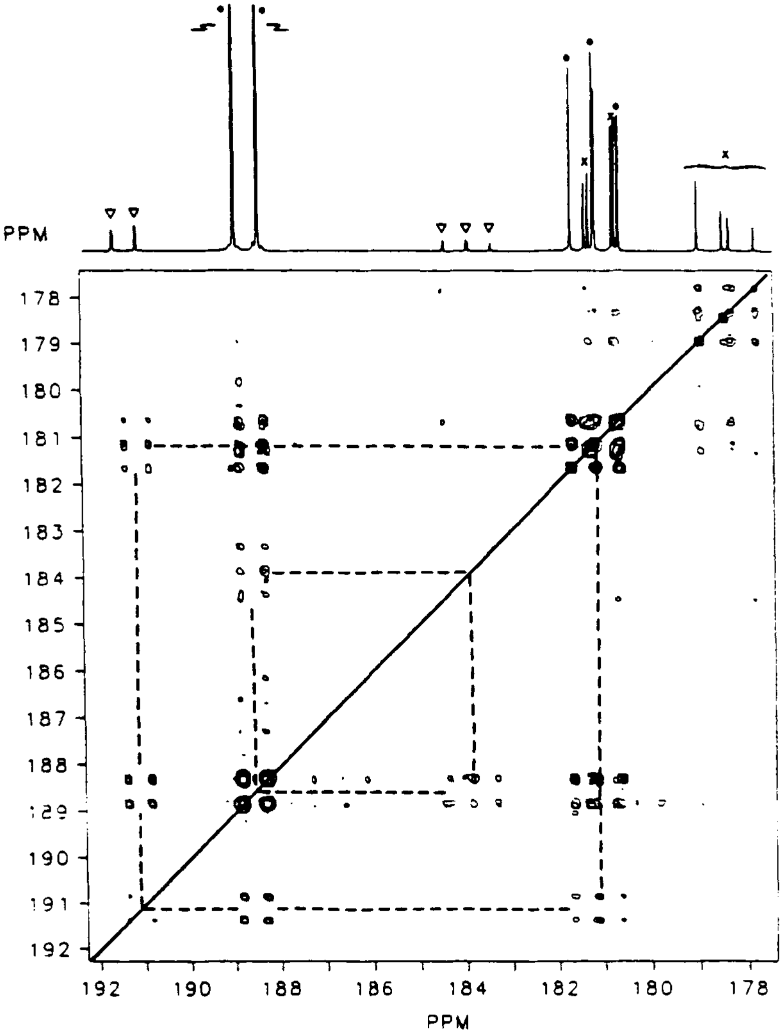


FIGURE 1 2-D ^{31}P contour map for $\mathrm{Cr(CO)_2(CS)[(MeO)_3P]_3}$ in deuterotoluene at 61°C on a Varian XL-300 spectrometer; an NOE accordian pulse sequence was employed with $\kappa = 30$. All three isomers exhibit an $\mathrm{AB_2}$ coupling pattern (chemical shifts are relative to $\mathrm{H_3PO_4}$ as external standard): ▽ = *mer* II P_2, P_3 (d) 191.4 ppm, P_1(t) 184.0 ppm (J = 64 Hz); ● = *mer* I P_2, P_3 (d) 188.6 ppm, P_1(t) 181.2 ppm (J = 64 Hz); × = *fac* P_2, P_3(d) 181.1 ppm, P_1(t) 178.5 ppm (J = 72 Hz). Reproduced from Ref. 28 with permission.

that the correlations observed can be used to establish the mechanistic pathway followed in the *mer-I* to *mer-II* isomerization. The correlations show unambiguously that the trigonal-prismatic (Bailar) twist is involved rather than the bicapped-tetrahedral twist (Fig. 2). This is the first time that it has been possible to show definitively the precise mechanism in the intramolecular isomerization of an octahedral complex. If the alternative bicapped tetrahedron mechanism had been involved, there would have been no change in the coupling pattern for the phosphorus nuclei in the two isomers, contrary to the observed correlation map. The *mer-I* to *fac* or *fac* to *mer-II* rearrangements can be envisaged to occur

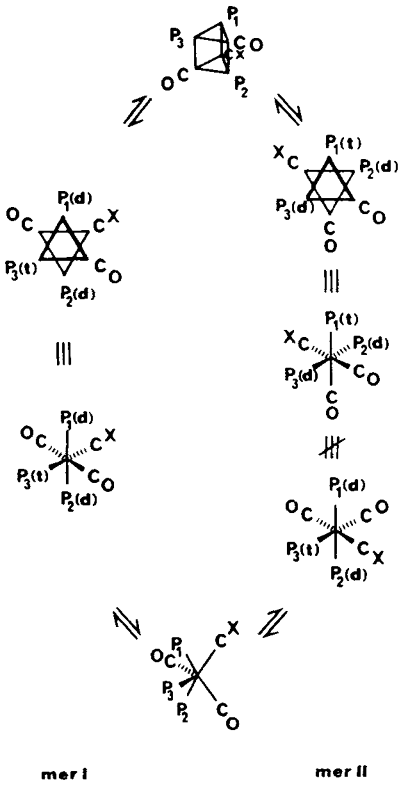


FIGURE 2 Reproduced from Ref. 28 with permission.

by similar twists involving trigonal-prismatic intermediates. Similar results have also been obtained for complexes containing chelated phosphine ligands, e.g., $Cr(CO)_2(CX)(triphos)$ [triphos = $PhP(CH_2CH_2PPh_2)_2$].[32]

The success of the 2-D experiments lies in the distinct electronic bonding differences between the CO and CX ligands giving rise to different ^{31}P NMR chemical shifts for the three isomers. It appears that the *fac* isomers are formed initially but these quickly isomerize to the more thermodynamically stable *mer-I* isomers.[26,33] This may be the reason for the lack of expected catalytic activity of the $(\eta^6\text{-}PhCO_2Me)Cr(CO)_2(CS)$ complex since it appears that the *fac*-$Cr(CO)_3(S)_3$ complexes, formed by arene displacement, are necessary for catalytic hydrogenation to take place.[2]

CONCLUSION

The arene displacement reactions of (η^6-arene)chromium(0) carbonyl complexes are much more complicated than was originally suspected. The latest work has demonstrated the possibility of dimeric intermediates involving Cr=Cr bonds being implicated in the mechanisms. Moreover, the mechanisms of the reactions are now much better understood and these apparently simple metathetical substitution reactions can lead to some fascinating and important stereochemical consequences for non-rigid, octahedral organometallic complexes.

Acknowledgments

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