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Arene displacement in chromium chalcocarbonyl complexes by tertiary phosphorus ligands

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Abstract

Displacement of the arene in (η-arene)$Cr(CO)_2(CX)$ (arene = C_6H_6; $PhCO_2Me$; X = S, Se) by tertiary phosphite ligands (L = $(RO)_3P$; R = Me, Et, n-Bu, Ph) and tridentate tertiary phosphine ligands (L–L–L = triphos-U[$(Me)C(CH_2P(Ph)_2)_3$], triphos = [$(Ph_2PCH_2CH_2)_2PhP$]) affords a convenient synthetic route to new series of isomeric complexes of stoichiometry $Cr(CO)_2(CX)L_3$ and (L–L–L)$Cr(CO)_2(CX)$. The stereochemistries of these isomers have been established on the basis of their FT-IR (ν(CO) region) and ^{31}P NMR spectra. The influence of the different chalcocarbonyl ligands (CO, CS, CSe) on the positions of the ^{31}P resonances is discussed.

Introduction

The bonding properties of the thiocarbonyl (CS) and selenocarbonyl (CSe) ligands in transition-metal complexes have been compared extensively with those of CO and it is clear that the net electron-withdrawing capacities of the chalcocarbonyl ligands increase as CO < CS < CSe [1]. In view of the bonding differences between the three chalcocarbonyl ligands, the chemical behavior of thio- and seleno-carbonyl complexes and their carbonyl analogs would also be expected to differ. A striking example is the much greater ease of arene displacement from (η-arene)$Cr(CO)_2(CX)$ (X = S, Se) complexes than from their tricarbonyl counterparts [2]. $Cr(CO)_5(CS)$ can be prepared by heating (η-$PhCO_2Me$)$Cr(CO)_2(CS)$ under CO pressure (10 atm) at 65 °C for 5 h. These conditions are much milder than those required to produce $Cr(CO)_6$ from (η-$PhCO_2Me$)$Cr(CO)_3$ (65 °C, 20 atm CO, 6 days). The lability of the arene in the selenocarbonyl derivatives is even more pronounced; (η-$PhCO_2Me$)$Cr(CO)_2(CSe)$ reacts with CO at 10 atm pressure in 1 h at 65 °C to yield $Cr(CO)_5(CSe)$. We have recently reported the results of a detailed kinetic study of the arene displacement reactions of (η-$PhCO_2Me$)$Cr(CO)_2(CX)$ (X = S, Se) by

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$(MeO)_3P$ [3], and also some X-ray structural work on the products [4]. These reactions also proceed under much milder conditions than the corresponding reactions of their tricarbonyl analogues.

The enhanced arene lability in the thio- and seleno-carbonylchromium complexes should afford a convenient route to the synthesis of a variety of new chalcocarbonyl derivatives. We report here the results of such an investigation for the arene displacement reactions of (η-arene)$Cr(CO)_2(CX)$ (X = S, Se) complexes with monodentate and tridentate tertiary phosphine and phosphite ligands. Our interest in arene displacement reactions of chromium complexes stems chiefly from the fact that the parent tricarbonyl complexes are useful homogeneous catalysts for the isomerization of dienes in coordinating solvents such as tetrahydrofuran [5]. Displacement of the arene ligands is a crucial step in the catalytic cycle.

Experimental

The tertiary phosphites were purchased from Aldrich Chemical Co., with the exception of $(C_6H_{11}O)_3P$, which was obtained from Strem Chemicals. CSe_2, $Cr(CO)_6$, and the tridentate tertiary phosphine ligands, bis(2-diphenylphosphinoethyl)phenylphosphine (triphos = $[(Ph_2PCH_2CH_2)_2PhP]$) and 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos-U = $[(Me)C(CH_2P(Ph)_2)_3]$), were purchased from Strem Chemicals. (cht)$Cr(CO)_3$ (cht = cycloheptatriene, C_7H_8) was either prepared by the literature method [6], or purchased from Strem Chemicals.

All synthetic reactions and manipulations were performed under an atmosphere of prepurified N_2. The solvents were freshly distilled under N_2 over sodium strips prior to use, with the exception of 1,2-dichloroethane and CS_2, which were distilled over $CaCl_2$ and molecular sieves, respectively.

Chromatographic separation of the reaction products was achieved by column chromatography (silica gel, 60–200 mesh under an N_2 atmosphere or on preparative TLC plates (1 mm) prepared from a slurry of 80 g silica gel G (Macherey, Nagel & Co., 5160 Durn, West Germany) and 180 ml water. The plates were activated prior to use by heating them at 110 ° C for 1 h. Microanalyses were performed by Guelph Chemical Laboratories, Guelph, Ontario, Canada.

FT-IR spectra were recorded on a Nicolet 6000 spectrometer (32 scans, 1 cm^{-1} resolution; mercury-cadmium-telluride detector). Carbon-13 and ^{31}P NMR spectra were measured on a Varian XL-200 or XL-300 spectrometer equipped with a 5-mm broad-band probe. The chemical shifts reported are relative to Me_4Si (^{13}C) and 85% H_3PO_4 (^{31}P).

Preparation of $Cr(CO)_2(CX)[(RO)_3P]_3$ (X = S, Se) (R = Me, Et, n-Bu, Ph). The $Cr(CO)_2(CX)[(RO)_3P]_3$ complexes were prepared in quantitative yields according to the literature procedure for $Cr(CO)_2(CX)[(MeO)_3P]_3$ [3,4], and the solid yellow materials were identified by the similarity of their FT-IR (ν(CO) region) and NMR (^{13}C, ^{31}P) spectra to the $(MeO)_3P$ derivatives.

Preparation of (triphos-U)$Cr(CO)_2(CS)$. Triphos-U (985 mg, 1.58 mmol) and (η-C_6H_6)$Cr(CO)_2(CS)$ (197 mg, 0.855 mmol) were dissolved under N_2 in 25 ml of toluene. The reaction mixture was heated at 90 ° C overnight and then the resulting solution was evaporated under reduced pressure, affording a yellow solid. The product was purified by TLC on silica gel plates using CS_2 as the moving phase. The yellow fraction was extracted with CH_2Cl_2 and evaporated to dryness. The solid obtained was dissolved in a minimal amount of benzene, and hexane was added slowly to precipitate bright yellow crystals. Anal. Found: C, 67.87; H, 5.25. $C_{44}H_{39}O_2P_3SCr$ calcd.: C, 68.04; H, 5.02%. IR $(CH_2Cl)_2$: ν(CO) 1927.7s, 1866.1s cm^{-1}; ν(CS) 1190m cm^{-1}.

Preparation of (triphos)Cr(CO)$_2$(CS). Triphos (1.02 g, 1.91 mmol) and (η-C_6H_6)Cr(CO)$_2$(CS) (203 mg, 0.88 mmol) were dissolved in toluene and heated at 95 °C overnight while stirring under N_2. The workup was analogous to the procedure described above for (triphos-U)Cr(CO)$_2$(CS). Attempts to separate the isomers of (triphos)Cr(CO)$_2$(CS) by TLC using various eluents (1,2-dichloroethane/hexane, 3/1; benzene/CS_2, 2/1; ethyl acetate/petroleum ether, 3/2) were unsuccessful. Yield 570 mg (94%). Anal. Found: C, 64.24; H, 5.02. $C_{37}H_{33}O_2P_3Cr$ calcd.: C, 64.66; H, 4.85%. IR (CH_2Cl_2): ν(CO) 1924.0s, 1860.9s cm^{-1}; ν(CS) 1191.4m cm^{-1}. ^{31}P NMR (isomers A and A*) 67.4 (dd, $I = 1$), 79.8 (dd, $I = 1$), 107.5 ppm (dd, $I = 1$), isomer B 100.9 (t, $I = 1$), 71.9 ppm (d, $I = 2$).

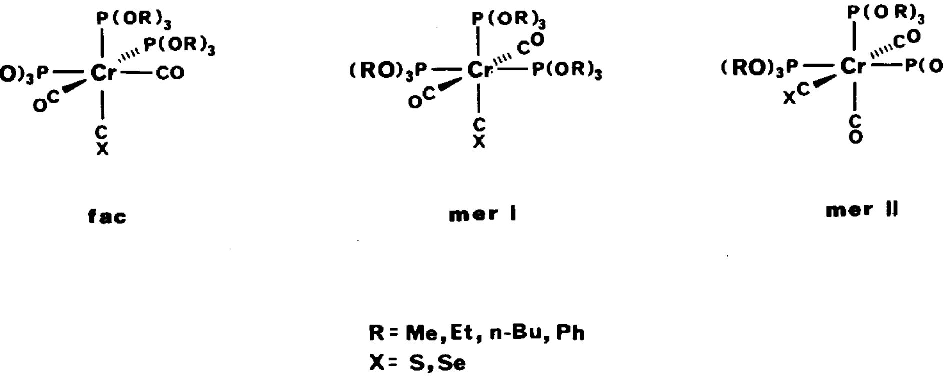
Preparation of (L–L–L)Cr(CO)$_2$(CSe) (L–L–L = triphos-U, triphos). These yellow, crystalline complexes were prepared in excellent yields (> 90%) according to the methods outlined above for the corresponding thiocarbonyl derivatives. They were identified by FT-IR (ν(CO) region) and NMR (^{13}C, ^{31}P) spectra.

Preparation of Cr(CO)$_3$[(RO)$_3$P]$_3$ (R = Me, Et, n-Bu, Ph) and (L–L–L)Cr(CO)$_3$ (L–L–L = triphos and triphos-U). These complexes were prepared in high yields (> 90%) from (cht)Cr(CO)$_3$ by the same procedures as described above for the corresponding thio- and seleno-carbonyl derivatives.

Results and discussion

Reactions of (η-Arene)Cr(CO)$_2$(CX) with monodentate tertiary phosphite ligands

Arene displacement from (η-arene)Cr(CO)$_2$(CX) complexes by tertiary phosphites yields the Cr(CO)$_2$(CX)[(RO)$_3$P]$_3$ derivatives, for which there are three geometrical isomers possible (Scheme 1). We have previously shown by X-ray diffraction that the *mer*-I isomer is the major product when R = (MeO)$_3$P [4]. The FT-IR and NMR spectra obtained in the present work indicate that the crude reaction products (prior to TLC purification) contain principally the *mer*-I isomer, but there is also a small amount of another isomer.



Scheme 1. Geometrical isomers for Cr(CO)$_2$(CX)[(RO)$_3$P]$_3$ complexes.

The CO stretching region of the IR spectrum of the crude product obtained in the synthesis of $Cr(CO)_2(CSe)[(MeO)_3P)_3]_3$ (Fig. 1) exhibits, in addition to the peaks of *mer*-I-$Cr(CO)_2(CSe)[(MeO)_3P)_3]_3$ (1980w, 1903vs cm^{-1}), a weak peak at 1962 cm^{-1}. Subtraction of the spectrum of the pure *mer*-I product from this spectrum reveals a residual peak at 1903 cm^{-1} of comparable intensity to that at 1957 cm^{-1} as well as a peak in the ν(CSe) region at 1018 cm^{-1}. These data indicate the presence of a small amount of either the *fac* or *mer*-II isomer. In the ^{13}C NMR spectrum of the crude $Cr(CO)_2(CSe)[(MeO)_3P]_3$ (Fig. 2), the ^{13}CO and the ^{13}CSe resonances of the *mer*-I isomer are assigned to the quartet at 223.8 ppm and the triplet of doublets at 356.4 ppm, respectively. In addition to these peaks, there is a single ^{13}CO resonance (δ 225.5 ppm) split into a multiplet and a ^{13}CSe resonance (δ 354.8 ppm) split into a doublet of triplets. It is well established that chalcocarbonyl resonances exhibit a downfield shift when they are *trans* to a stronger σ-donor or a weaker π-acceptor ligand than CO [7,8]. On this basis, the *mer*-II isomer would be expected to exhibit a selenocarbonyl resonance at higher field than observed for the *mer*-I isomer and two distinct carbonyl resonances, one at higher field than that of the *mer*-I isomer for the CO *trans* to the CSe ligand, and the other at lower field for the CO *trans* to the phosphite group. Therefore, the ^{13}C NMR data are inconsistent with the identification of the minor product as the *mer*-II isomer. For the *fac* isomer, on the other hand, a single CO resonance situated at lower field than that of the *mer*-I isomer is expected, while the thiocarbonyl resonance is anticipated to appear at higher field on the grounds that the CO groups should remove a larger share of the electron density donated by the tertiary phosphites to the metal in the *fac* isomer (CO *trans* to phosphite) than in the *mer*-I case (CO *cis* to phosphite).

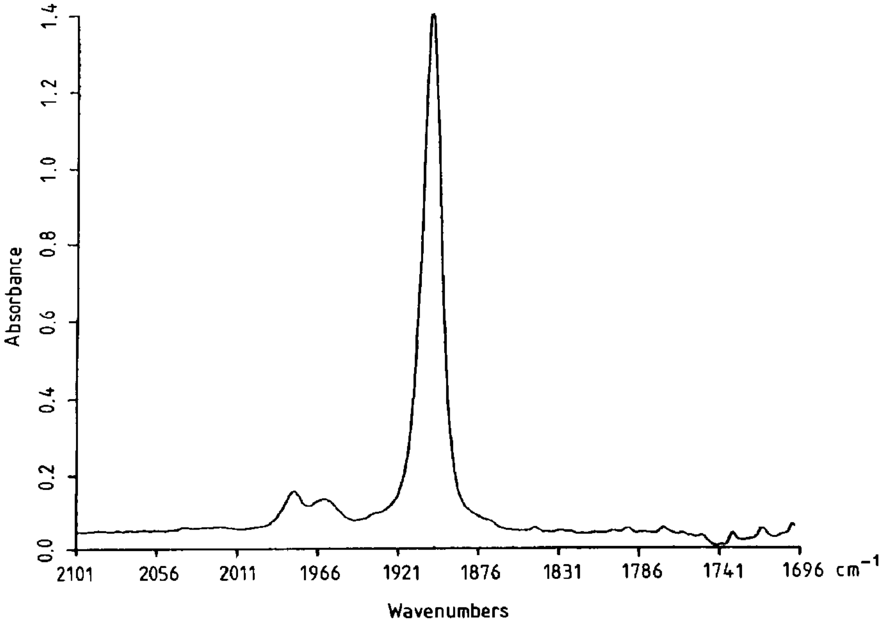


Fig. 1. FT-IR spectra (in CS_2 solution) in the ν(CO) region of the crude reaction product from the reaction of (η-$PhCO_2Me$)$Cr(CO)_2(CSe)$ with $(MeO)_3P$. The spectra and the reaction products using other tertiary phosphites exhibit identical band intensity profiles.

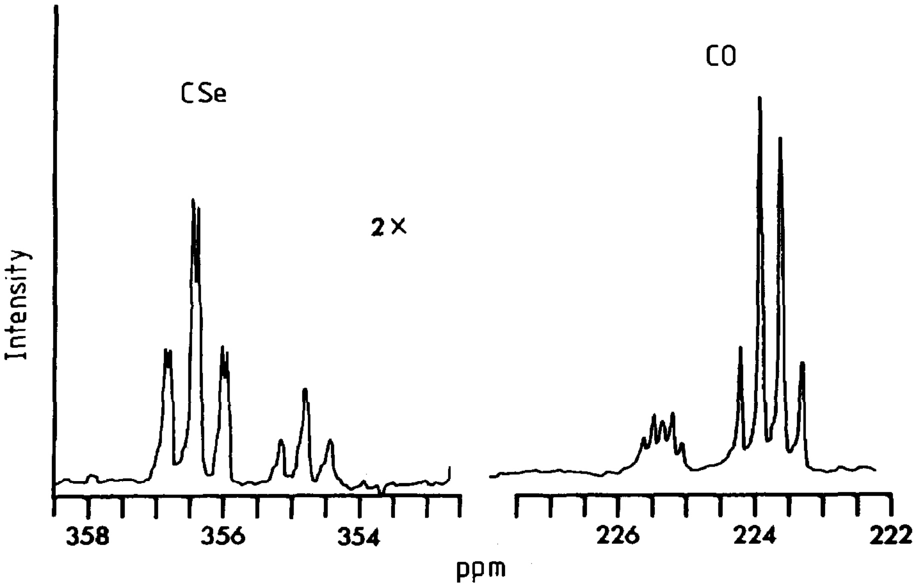


Fig. 2. The CSe and CO resonances in the ^{13}C NMR spectrum (in C_6D_6 solution) of a mixture of the *fac* and *mer*-I isomers of $Cr(CO)_2(CSe)[(MeO)_3P]_3$. Conditions: Varian-XL-300 FT-NMR spectrometer operating at 75.43 MHz, ^1H-decoupled; sweep width, 30000 Hz; offset, 7100 Hz; flip angle, 20°; repetition time, 0.6 s; 2624 scans. Sample contained a small amount of 0.1 *M* $Cr(acac)_3$.

The FT-IR (ν(CO) region) and ^{31}P NMR spectra for a series of *fac* and *mer*-I $Cr(CO)_2(CX)[(RO)_3P]_3$ (X = S, Se) isomers containing different tertiary phosphite ligands are given in Tables 1 and 2, respectively. These complexes were all prepared by displacement of the arenes from (η-arene)$Cr(CO)_2(CX)$ with tertiary phosphites. Spectral data for the analogous tricarbonyl complexes are also included in the tables.

The ν(CO) modes in the FT-IR spectra of the $Cr(CO)_2(CX)[(RO)_3P]_3$ (X = O, S) complexes demonstrate the greater effectiveness of the CS group in decreasing the net electron density at a metal centre compared to CO. This is illustrated clearly by the increase in the mean values of the wavenumbers for the CO stretching modes in the thiocarbonyl complexes because of the decreased backdonation from the metal to the π^* orbitals of the CO groups [1].

Selenocarbonyl-transition metal complexes are quite rare [1]. The compounds listed in Tables 1 and 2 are the first examples of transition metal complexes, triple the number of selenocarbonyls known for the group 6B metals, and provide further support for the superiority of CSe to either CS or CO in depleting electron density from low-oxidation state metals and other coordinated ligands. Proof of this comes from the higher wavenumber values obtained for the mean of the ν(CO) modes.

The poor correlations obtained previously between ν(CX) (X = S, Se) (in cm^{-1}) and the σ-donor/π-acceptor properties of the other bonded ligands in chalcocarbonyl complexes have been attributed to appreciable mixing of the ν(CX) and ν(M–CX) modes [9]. Nevertheless, a qualitative trend is evident in the present work for the ν(CX) modes of the *fac* and *mer*-I isomers as the σ-donor/π-acceptor properties of the phosphite ligands are varied. This trend seems to parallel the net electron density at the metal rather than the stereochemistry of the ligands relative

Table 1

ν(CX) modes (cm^{-1}) of the *fac*- and *mer*-$Cr(CO)_2(CX)[(RO)_3P]_3$ (X = O, S, Se) derivatives in CS_2 solution

Complex	*fac* isomers [a]			*mer* isomers [b]		
	ν(CO)	Mean ν(CO)	ν(CS) or ν(CSe)	ν(CO)	Mean ν(CO)	ν(CS) or ν(CSe)
$Cr(CO)_3[(MeO)_3P]_3$	1962s 1875s	1919		1979vw 1875vs	1927	
$Cr(CO)_2(CS)[(MeO)_3P]_3$	1957s 1895s	1926	1199m	1974w 1895vs	1935	1199m
$Cr(CO)_2(CSe)[(MeO)_3P]_3$	1962s 1903s	1933	1018m	1980w 1903vs	1942	1018m
$Cr(CO)_3[(EtO)_3P]_3$	1957s 1867s	1912		1973w 1867vs	1920	
$Cr(CO)_2(CS)[(EtO)_3P]_3$	1950s 1889s	1920	1193m	1970w 1889vs	1930	1193m
$Cr(CO)_2(CSe)[(EtO)_3P]_3$	1957s 1898s	1928	1016m	1975w 1898vs	1937	1016m
$Cr(CO)_3[(n\text{-}BuO)_3P]_3$	1956s 1867s	1912		1973w 1867vs	1920	
$Cr(CO)_2(CS)[(n\text{-}BuO)_3P]_3$	1950s 1889s	1920	1192m	1971w 1889vs	1930	1192m
$Cr(CO)_2(CSe)[(n\text{-}BuO)_3P]_3$	1956s 1897	1927	1018m	1974w 1897vs	1936	1018m
$Cr(CO)_3[(PhO)_3P]_3$	1982s 1910s	1946		2004w 1910vs	1957	
$Cr(CO)_2(CS)[(PhO)_3P]_3$	1973s 1929s	1951	1220s	1987w 1929vs	1958	1220s
$Cr(CO)_2(CSe)[(PhO)_3P]_3$	1974s 1940s	1957	1023m	1996w 1940s	1968	1023m

[a] The assignments for the ν(CO) modes in order of decreasing energy, based on the local symmetries of the $Cr(CO)_3$ (C_{3v}) and $Cr(CO)_2(CX)$ (X = S, Se) (C_s) moieties, are a_1 and e for the former and a' and a'' for the latter. [b] *mer* = *mer*-I for the thio- and seleno-carbonyl complexes. For *mer*-$Cr(CO)_3L_3$, the ν(CO) modes are $2a_1 + b_1$ (for C_{2v} local symmetry), with one of the a_1 modes assigned to the higher-energy peak; the a_1 and b_1 components of the lower-energy peak were not resolved. For the *mer*-I isomers, $\nu(CO) = a_1 + b_1$ (for C_{2v} local symmetry); the a_1 mode is assigned to the higher-energy peak.

Table 2

^{31}P NMR data [a] for $Cr(CO)_2(CX)[(RO)_3P]_3$ derivatives (X = O, S, Se) [a,b]

Complex	^2J(PP) (Hz)	$\delta(^{31}P)$ (d, $I = 2$) (ppm)	$\delta(^{31}P)$ (t, $I = 1$) (ppm)
mer isomers			
$Cr(CO)_3[(MeO)_3P]_3$	64	197.4	189.1
$Cr(CO)_2(CS)[(MeO)_3P]_3$	65	188.6	181.2
$Cr(CO)_2(CSe)[(MeO)_3P]_3$	64	184.9	177.5
$Cr(CO)_3[(EtO)_3P]_3$	60	193.3	184.9
$Cr(CO)_2(CS)[(EtO)_3P]_3$	65	186.3	177.4
$Cr(CO)_2(CSe)[(EtO)_3P]_3$	64	181.6	172.5
$Cr(CO)_3[(n\text{-}BuO)_3P]_3$	59	193.0	184.6
$Cr(CO)_2(CS)[(n\text{-}BuO)_3P]_3$	64	186.2	177.2
$Cr(CO)_2(CSe)[(n\text{-}BuO)_3P]_3$	64	181.5	172.8
$Cr(CO)_3[(PhO)_3P]_3$	65	177.7	168.6
$Cr(CO)_2(CS)[(PhO)_3P]_3$	62	170.5	162.6
$Cr(CO)_2(CSe)[(PhO)_3P]_3$	62	166.0	159.9
fac isomers			
$Cr(CO)_2(CS)[(MeO)_3P]_3$	72	180.7	178.2
$Cr(CO)_2(CSe)[(MeO)_3P]_3$	72	178.4	174.7
$Cr(CO)_2(CSe)[(PhO)_3P]_3$	68	160.1	157.0

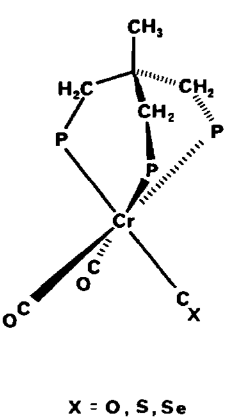
[a] In $C_6H_5CD_3$ solution; chemical shifts are in ppm (±0.1 ppm) downfield from 85% H_3PO_4. [b] *mer* = *mer*-I for the thio- and seleno-carbonyl complexes.

to each other. A similar observation has also been made for *cis*- and *trans*-$W(CO)_4(CS)(L)$ derivatives [10].

Table 2 summarizes the ^{31}P NMR data obtained for the *mer*-I $Cr(CO)_2(CX)[(RO)_3P]_3$ (X = O, S, Se; R = Me, Et, n-Bu and Ph) complexes. A comparison of the ^{31}P resonance for the two phosphorus atoms *trans* to each other in the chalcocarbonyl triad reveals an upfield shift of about 7 ppm for the CS derivative and about 11.5 ppm for the CSe one, when compared to the corresponding tricarbonyl. This observation is consistent with a net decrease in electron density at the metal centre available for donation to the *d* orbitals of the phosphorus atoms in view of the established acidity trend for chalcocarbonyl ligands (CSe > CS > CO). An increase in electron density donation from the phosphorus atoms to the relatively electron-deficient metal in the thio- and seleno-carbonyl complexes may also contribute to the observed effect. The signal for the phosphorus atom *trans* to the CX (X = O, S, Se) ligand is shifted further upfield from that for the two *trans* phosphorus atoms. A similar trend is observed in the shift towards higher fields for the phosphorus resonance with increasing π-acidity of the *trans* ligand in the order CSe > CS > CO. The magnitude of the difference is comparable to that for the two *trans* phosphorus atoms.

Reactions of (η-arene)$Cr(CO)_2(CX)$ with tridentate tertiary phosphine ligands

Treatment of (η-arene)$Cr(CO)_2(CX)$ (X = S, Se) with triphos-U yields the *fac*-(triphos-U)$Cr(CO)_2(CX)$ derivatives (Scheme 2). The associated FT-IR (ν(CO) region) and ^{31}P NMR data are given in Tables 3 and 4, respectively, together with data for the corresponding tricarbonyl complex. As expected, the mean IR ν(CO) frequency shifts to higher wavenumber on descending the chalcocarbonyl triad. The ^{31}P NMR spectrum of the *fac*-(triphos-U)$Cr(CO)_3$ complex exhibits only one signal since the three phosphorus atoms are equivalent. In the case of (triphos-U)$Cr(CO)_2(CX)$ (X = S, Se) the different environments of the phosphorus atoms result in a doublet and a triplet splitting pattern where the ^{31}P signal of the phosphorus atom *trans* to CX (triplet) is further upfield than the ^{31}P resonance (doublet) of the two phosphorus atoms *trans* to CO. Comparison of the ^{31}P



X = O, S, Se
P = P Ph_2

Scheme 2. Geometrical isomer for (triphos-U)$Cr(CO)_2(CX)$ complexes.

Table 3

ν(CX) modes (cm^{-1}) of (L–L–L)Cr(CO)$_2$(CX) derivatives (X = O, S, Se; L–L–L = tridentate tertiary phosphine) in CS$_2$ solution

Complex	ν(CO)	ν(CS) or ν(CSe)
(triphos-U)Cr(CO)$_3$	1931s 1830s	
(triphos-U)Cr(CO)$_2$(CS)	1929s 1871s	1190m
(triphos-U)Cr(CO)$_2$(CSe)	1937s 1881s	1031s
(triphos-U)Cr(CO)$_3$	1934s 1844s	
(triphos)Cr(CO)$_2$(CS) [a]	1924s 1861s	1191m
(triphos)Cr(CO)$_2$(CSe) [a]	1940s 1885s	1037s

[a] The peaks due to isomers **A** and **B** were not resolved.

resonance for (triphos-U)Cr(CO)$_3$ with that of the corresponding resonance of the phosphorus atoms *trans* to CO in (triphos-U)Cr(CO)$_2$(CSe) indicates an upfield shift of 8 ppm in the selenocarbonyl complex. The phosphorus *trans* to the CSe is approximately 5 ppm upfield from the other two phosphorus atoms *trans* to CO in the same complex.

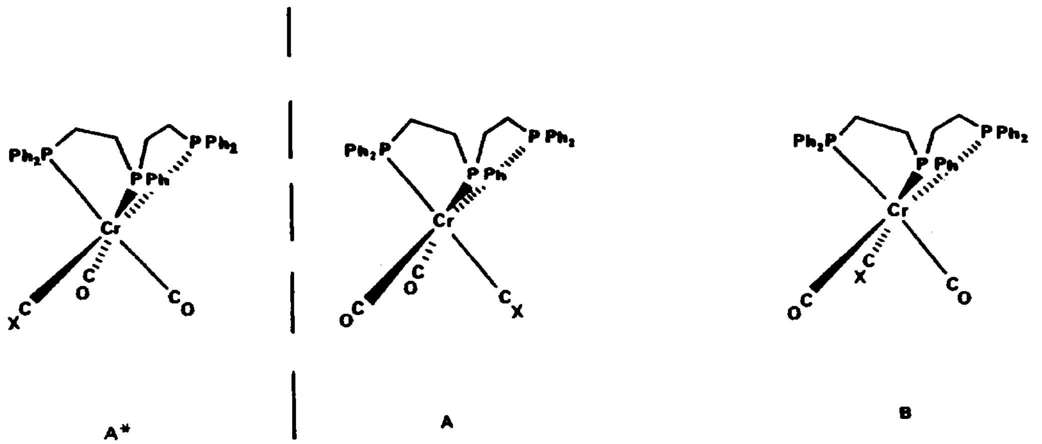
Arene displacement by triphos from (η-arene)Cr(CO)$_2$(CX) affords three different types of *fac* isomer (**A**, **A*** and **B**, where **A*** is an enantiomer of **A**; Scheme 3) that are not available to the parent tricarbonyl complex. The FT-IR spectra of the complexes in the ν(CO) region display only two strong absorptions (Fig. 3) with mean values at higher energies than those for the parent tricarbonyl complexes [11]. Moreover, the mean ν(CO) value in the case of the selenocarbonyl derivative is

Table 4

^{31}P NMR data for (L–L–L)Cr(CO)$_2$(CX) derivatives (X = O, S, Se; L–L–L = tridentate tertiary phosphine) [a]

Complex	J(PP) (Hz)	δ(^{31}P) (ppm)
triphos-U		−24.8
(triphos-U)Cr(CO)$_3$		39.6
(triphos-U)Cr(CO)$_2$(CSe)	31	31.5 (d, $I = 2$)
		26.9 (t, $I = 1$)
triphos	28	−11.7 (d, $I = 2$)
		−15.6 (t, $I = 1$)
(triphos)Cr(CO)$_3$	12	84.0 (d, $I = 2$)
		115.2 (t, $I = 1$)
(triphos)Cr(CO)$_2$(CS) (**A**)	10, 24	67.4 (dd, $I = 1$)
		79.8 (dd, $I = 1$)
		107.5 (dd, $I = 1$)
(triphos)Cr(CO)$_2$(CS) (**B**)	9	71.9 (d, $I = 2$)
		100.9 (t, $I = 1$)
(triphos)Cr(CO)$_2$(CSe) (**A**)	10, 24	64.4 (dd, $I = 1$)
		76.9 (dd, $I = 1$)
		104.0 (dd, $I = 1$)
(triphos)Cr(CO)$_2$(CSe) (**B**)	10	68.6 (d, $I = 2$)
		96.7 (t, $I = 1$)

[a] In CD$_2$Cl$_2$ solution; chemical shifts are in ppm (±0.1 ppm) with positive values downfield from 85% H$_3$PO$_4$.



Scheme 3. Geometrical and optical isomers for (triphos)Cr$(CO)_2$(CX).

higher than that for the thiocarbonyl derivative. The (CX) (X = S, Se) modes for the **A** and **B** isomers appear as one unresolved peak.

Isomer **A** (and **A***) of (triphos)Cr$(CO)_2$(CX) (X = S, Se) is expected to exhibit three ^{31}P NMR signals since the two terminal phosphorus atoms of the triphos ligand are *trans* to different ligands and the bridging phosphorus atom is in a different environment from the other two phosphorus atoms in the free ligand. Isomer **B** with the bridging phosphorus atom *trans* to the CX ligand is expected to have two signals since the terminal phosphorus nuclei experience identical environments. The isomers were detected in the ^{31}P spectrum in a 4/1 ratio (**A**/**B**) (Fig. 4).

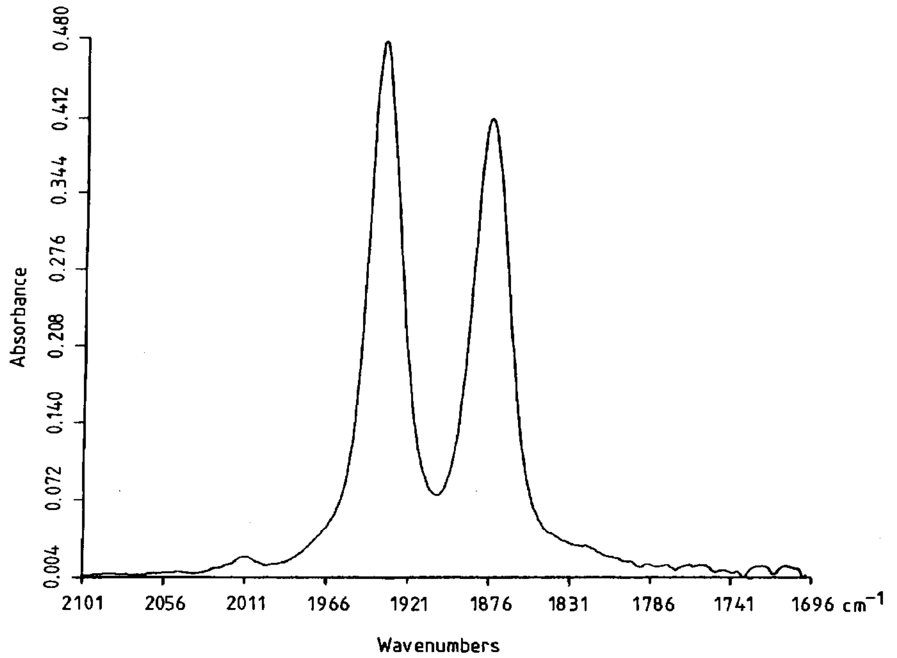


Fig. 3. ν(CO) region in the FT-IR spectra in CH_2Cl_2 solution of (triphos)Cr$(CO)_2$(CSe).

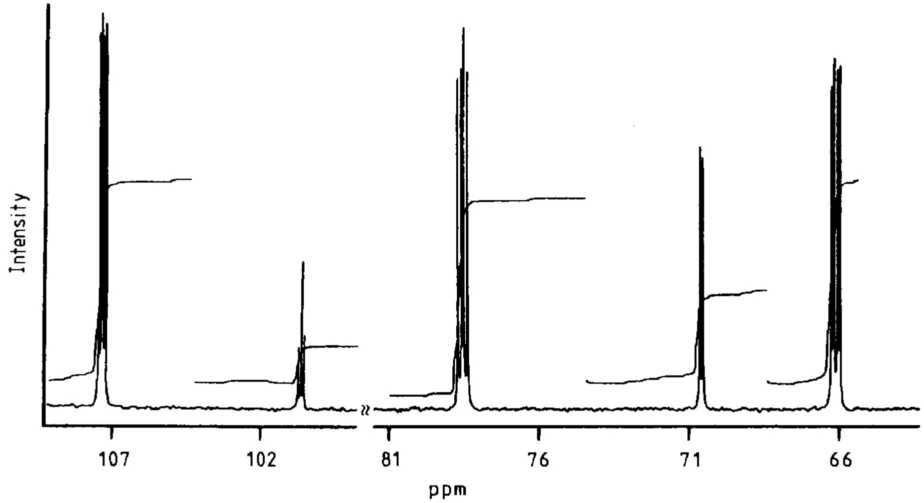


Fig. 4. ^{31}P NMR spectrum of (triphos)Cr(CO)$_2$(CSe) in $C_6D_5CH_3$ solution. Conditions: Varian XL-300 FT-NMR spectrometer operating at 121.42 MHz, ^{1}H-decoupled, sweep width, 6300 Hz; offset, 10200 Hz; flip angle, 66°; repetition time, 20 s; 200 scans.

The assignment of the resonances for isomer **A** was facilitated by comparison with the spectrum of the parent tricarbonyl which enabled the resonance due to the bridging phosphorus atom to be easily identified. The resonances due to the terminal phosphorus atoms were assigned on the basis of the trend observed for ^{31}P resonances in the chalcocarbonyl complexes presented in this paper. Thus, the resonance at higher field was assigned to the phosphorus atom *trans* to CX (X = S, Se). The ^{31}P NMR spectrum of isomer **B** was directly assigned by comparison with that of the parent (triphos)Cr(CO)$_3$ complex [12].

Conclusions

Two new series of chalcocarbonyl chromium complexes, Cr(CO)$_2$(CX)[(RO)$_3$P]$_3$ and (L–L–L)Cr(CO)$_2$(CX) (X = S, Se), have been prepared by the facile displacement of arene ligands from (η-arene)Cr(CO)$_2$(CX). Carbon-13 and ^{31}P NMR spectroscopy, in particular, have proved invaluable in determining the stereochemistry of the different isomeric products. Access to these new series of derivatives was made possible by the strong net electron-withdrawing capacities of the CS and CSe ligands resulting in a weakening of the Cr–arene bond.

Our interest is presently focused on the mechanism of isomerization of the new complexes. Preliminary results for Cr(CO)$_2$(CX)[(MeO)$_3$P]$_3$ (X = S, Se) have indicated that the *fac* and *mer*-I isomers and the *mer*-I and *mer*-II isomers interconvert through non-bond breaking processes [13]. Further studies of the intramolecular isomerization of Cr(CO)$_2$(CX)[(RO)$_3$P]$_3$ and (L–L–L)Cr(CO)$_2$(CX) (X = S, Se) series will be undertaken.

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