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REACTIVITY OF COORDINATED $Ph_2P(C_5H_5)$. PREPARATION OF $M(CO)_{6-n}[Ph_2P(C_5H_4Tl)]_n$ COMPLEXES ($M = Cr, Mo$; $n = 1,2$)

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Abstract—The interaction of $C_7H_8Cr(CO)_4$ with two equivalents of $Ph_2P(C_5H_5)$ in hexane at 0°C gives *trans*-$Cr(CO)_4[Ph_2P(C_5H_5)]_2$ (**I**) in high yield (80%). In $CDCl_3$ at 30°C, **I** isomerizes to *cis*-$Cr(CO)_4(Ph_2PC_{10}H_{10}PPh_2)$ (**II**) quantitatively. Compound **II** can also be prepared in high yield (85%) by the interaction of *trans*-$Cr(CO)_4(Ph_2PCl)_2$ with two equivalents of $Tl(C_5H_5)$ in refluxing toluene. Treatment of $M(CO)_6$ ($M = Cr, Mo$) with one equivalent of trimethylamine N-oxide in THF followed by the addition of one equivalent of $Ph_2P(C_5H_4Tl)$ affords $M(CO)_5[Ph_2P(C_5H_4Tl)]$ (**III**, $M = Cr$; **IV**, $M = Mo$) and $M(CO)_4[Ph_2P(C_5H_4Tl)]_2$ (**V**, $M = Cr$; **VI**, $M = Mo$). $M(CO)_4[Ph_2P(C_5H_4Tl)]_2$ adopts a *trans*- and a *cis*-configuration for chromium and molybdenum, respectively. The $M(CO)_4[Ph_2P(C_5H_4Tl)]_2$ complex can also be prepared conveniently either by the interaction of $C_7H_8M(CO)_4$ with two equivalents of $Ph_2P(C_5H_4Tl)$ or by the interaction of $M(CO)_4[Ph_2P(C_5H_5)]_2$ with two equivalents of $Tl(OEt)$ in THF.

The (diphenylphosphino)cyclopentadienyl anion $Ph_2P(C_5H_4)^-$ has been shown to be a very versatile reagent in organometallic synthesis. Its use as a difunctional reagent to bring two heterometal centres in close proximity has received considerable attention.[1] The preferred synthetic method has been to coordinate the C_5H_4 unit first to give an η^5-$C_5H_4PPh_2$ complex, and then to coordinate a second metal through the phosphine group. An alternative approach would be to coordinate the parent phosphine ligand $Ph_2P(C_5H_5)$ first, followed by deprotonation and coordination to a second metal via the cyclopentadienyl group. The first approach has been investigated extensively. However, relatively few studies have been carried out for the latter approach.

We recently reported the synthesis of *cis*-$Mo(CO)_4[Ph_2P(C_5H_5)]_2$ and showed that the coordinated $Ph_2P(C_5H_5)$ ligands when in a mutually *cis*-position underwent rapid Diels–Alder dimerization at room temperature producing the 1,3-bis(diphenylphosphine)dicyclopentadiene ligand.[2] In this paper, we report the isolation of the chromium analogy, *trans*-$Cr(CO)_4[Ph_2P(C_5H_5)]_2$, and the reactivities of the coordinated $Ph_2P(C_5H_5)$ ligands.

RESULTS AND DISCUSSION

Preparation and reactivity of trans-$Cr(CO)_4[Ph_2P(C_5H_5)]_2$ (I)

When $C_7H_8Cr(CO)_4$ was treated with two equivalents of $Ph_2P(C_5H_5)$ at 0°C in hexane, yellow crystals of the stoichiometry $Cr(CO)_4[Ph_2P(C_5H_5)]_2$ (**I**) were obtained in high yield (80%). The IR spectrum (KBr) of **I** exhibits an absorption at 1880s cm^{-1}. The absorption pattern is indicative of a *trans*-configuration for the four terminal carbonyl groups. The $^{31}P\{^1H\}$ NMR spectrum exhibits a singlet at δ20.0 ppm. In addition to the phenyl resonances, the ^1H NMR spectrum of **I** exhibits two multiplets of relative intensity 1 : 2 centred at δ6.84 and 6.49 ppm, respectively, in the olefinic proton region, and a broad singlet of relative intensity 2 centred at δ3.20 ppm in the aliphatic proton region for the cyclopentadienyl ring protons. The ^1H NMR chemical shifts are similar to those of the diphenyl(cyclopentadienyl)phosphine ligand of $Fe(CO)_4[Ph_2P(C_5H_5)]$.[3] Based on the above

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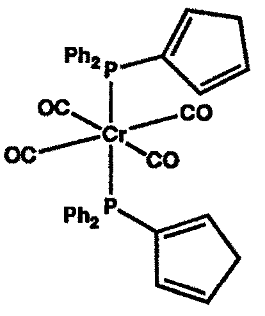
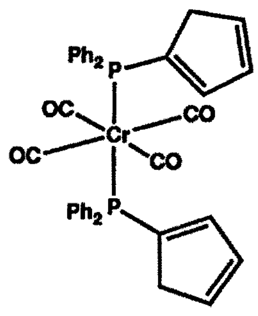
spectroscopic data, two structures are possible for **I**. These are **Ia** and **Ib** as shown below.



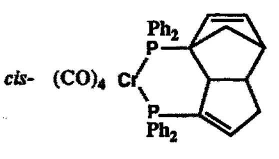
I$_a$



I$_b$

In contrast to *cis*-Mo(CO)$_4$[Ph$_2$P(C$_5$H$_5$)]$_2$ (**VIII**) **I** adopts a *trans*-configuration. This can be explained in terms of electronic and steric effects. For the Ph$_2$P(C$_5$H$_5$) ligand, which is a weaker π-acid than CO, the electronic effect favours the *cis*-isomer, whereas the steric effect favours the *trans*-isomer. The geometry adopted by M(CO)$_4$[Ph$_2$P(C$_5$H$_5$)]$_2$ (M = Cr, Mo) complexes depends on the relative importance of these two factors. In the absence of significant steric interaction, the electronic effect is the dominant factor and favours the formation of *cis*-M(CO)$_4$[Ph$_2$P(C$_5$H$_5$)]$_2$ complexes. Therefore, in the case of **VIII** where the central metal, molybdenum, is relatively large, the steric interaction between two mutually *cis*-Ph$_2$P(C$_5$H$_5$) ligands is relative weak and as a result, **VIII** adopts a mutually *cis*-configuration for the two Ph$_2$P(C$_5$H$_5$) ligands. The degree of congestion between two mutually *cis*-Ph$_2$P(C$_5$H$_5$) ligands increases as the size of the central metal decreases. In the case of **I** where the central atom, chromium, is relatively small, should the two Ph$_2$P(C$_5$H$_5$) ligands adopt a mutually *cis*-configuration, the two ligands would experience a strong steric interaction. For **I**, the steric interaction is so strong that it forces the two ligands to adopt a mutually *trans*-configuration. A similar observation is also reported for the M(CO)$_4$(Ph$_2$PCl)$_2$[4] complex, which adopts a *trans*- and a *cis*-configuration for chromium and molybdenum, respectively.

In hexane, **I** underwent isomerization at ambient temperature to give light green crystals of stoichiometry [Ph$_2$PC$_{10}$H$_{10}$PPh$_2$]Cr(CO)$_4$ (**II**) in 90% isolated yield. The IR spectrum (KBr) of **II** exhibits three absorptions at 2002 s, 1912 s and 1872 vs(br) cm^{-1}. The absorption pattern is indicative of a *cis*-configuration for the four terminal carbonyl groups. The ^{31}P{^{1}H} NMR spectrum of **II** exhibits two doublets of relative intensity 1 : 1 centred at δ41.0 (J = 34.2 Hz) and 56.1 ppm (J = 34.2 Hz), respectively. Compound **II** exhibits a very complicated ^{1}H NMR spectrum. In addition to the phenyl proton resonances, **II** exhibits three multiplets of relative intensity 1 : 1 : 1 centred at δ6.74, 6.12 and 5.13 ppm, respectively, in the olefinic proton region, and two multiplets, one ranged from δ1.62 to 2.87 ppm and the other centred at δ0.63 ppm of relative intensity 6 : 1, respectively, in the aliphatic proton region. The spectroscopic data of **II** are very similar to those of *cis*-[1,3-bis(diphenylphosphino)dicyclopentadiene](tetracarbonyl)molybdenum (**VII**), whose structure has recently been established by an X-ray diffraction study.[5] Thus, **II** can then be formulated as *cis*-[1,3-bis(diphenylphosphino)dicyclopentadiene](tetracarbonyl)chromium and has the following structure:

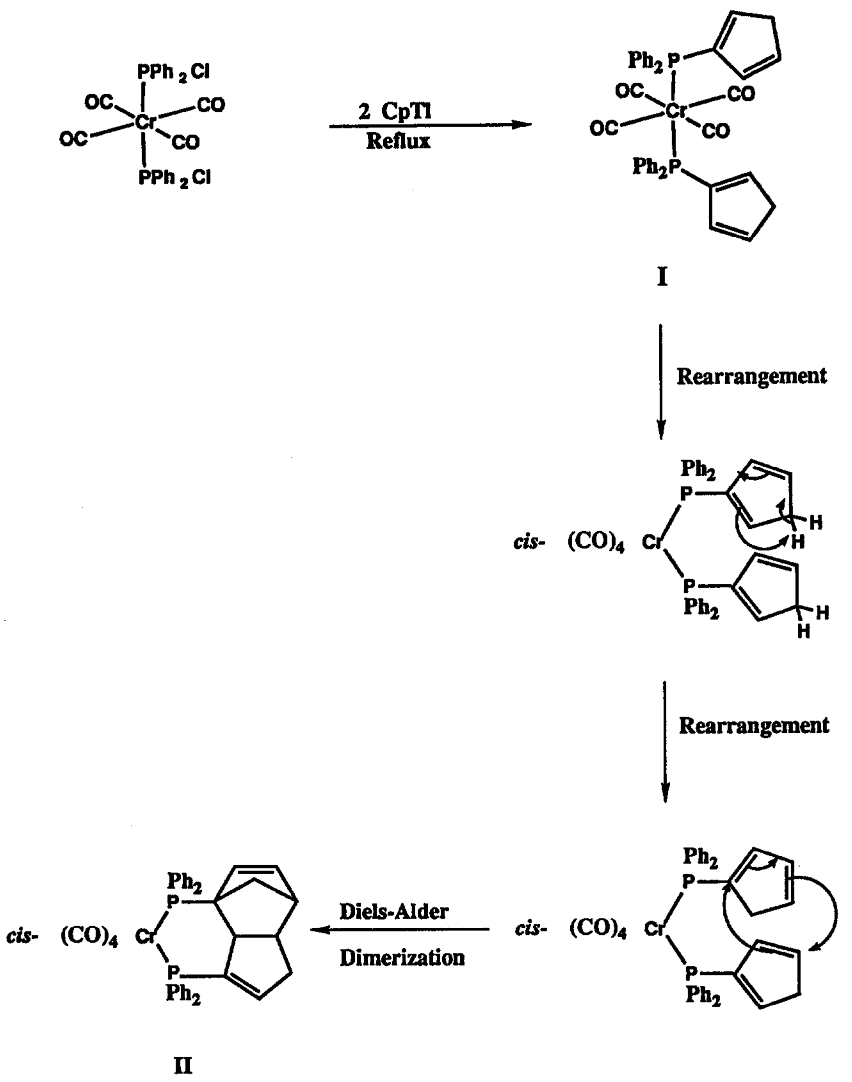


II

The result shows that rather than undergoing intermolecular Diels–Alder dimerization, the two Ph$_2$P(C$_5$H$_5$) ligands of **I** prefer to undergo intramolecular Diels–Alder dimerization to produce the 1,3-bis(diphenylphosphino)dicyclo-pentadiene ligand. This is further supported by the fact that Fe(CO)$_4$[Ph$_2$P(C$_5$H$_5$)][3] is stable to Diels–Alder addition and does not undergo intermolecular dimerization.

The formation of **II** is probably via the isomerization of **I** to the *cis*-configuration followed by intramolecular Diels–Alder dimerization as shown in Scheme 1. The course of the reaction was followed by ^{31}P{^{1}H} NMR spectroscopy. In CDCl$_3$ at 30°C, **I** isomerized to **II** quantitatively within 12 h. Other than the resonances due to **I** and **II**, no other resonances were observed. The inability to detect any other resonances suggests that as soon as **I** isomerized to the *cis*-configuration, the two Ph$_2$P(C$_5$H$_5$) ligands in the mutually *cis*-position underwent a facile intramolecular Diels–Alder dimerization to produce **II**. The intramolecular Diels–Alder dimerization process is so rapid that the intermediate cannot even be detected on the NMR time-scale at 30°C. This suggests that the rate determination step for the conversion of **I** to **II** is the *trans*- to *cis*-isomerization process of **I**.

Compound **I** reacted with two equivalents of Tl(OEt) to give a greenish yellow precipitate of stoichiometry Cr(CO)$_4$[Ph$_2$P(C$_5$H$_4$Tl)]$_2$ in high yield. The IR spectrum of the precipitate is identical



Scheme 1.

to that of *trans*-$Cr(CO)_4[Ph_2P(C_5H_4Tl)]_2$ (V) (*vide infra*).

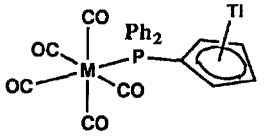
Interaction of trans-$Cr(CO)_4(Ph_2PCl)_2$ *with* $(C_5H_5)Tl$

When *trans*-$Cr(CO)_4(Ph_2PCl)_2$ was treated with two equivalents of $(C_5H_5)Tl$ in toluene at room temperature, no reaction was observed after 3 days. However, when the reaction was carried out in refluxed toluene for 16 h, **II** was isolated in 85% yield. Compound **II** is probably formed via the mechanism shown in Scheme 1. *Trans*-$Cr(CO)_4(Ph_2PCl)_2$ reacts with two equivalents of $(C_5H_5)Tl$ to produce the intermediate **I**. Compound **I** then isomerizes to the *cis*-configuration which undergoes hydrogen migration and finally intramolecular Diels–Alder dimerization to produce the final product **II**. A similar mechanism has been suggested for the formation of the analogous molybdenum complex.[2]

Preparation of $Cr(CO)_{6-n}[Ph_2P(C_5H_4Tl)]_n$ *complexes* (n = 1, 2)

(1) When $Cr(CO)_6$ was treated with one equivalent of trimethylamine N-oxide in THF followed by the addition of one equivalent of $Ph_2P(C_5H_4Tl)$, compounds of stoichiometry $Cr(CO)_5[Ph_2P(C_5H_4Tl)]$ (**III**) and $Cr(CO)_4[Ph_2P(C_5H_4Tl)]_2$ (**V**) were isolated in 60 and 10% yields, respectively. Compound **III** is insoluble in hexane, but soluble in benzene, toluene, diethyl ether, THF, $CHCl_3$ and CH_2Cl_2. However, it slowly decomposes in $CHCl_3$ and CH_2Cl_2. The IR spectrum (KBr) of **III** exhibits CO absorptions at 2060 m, 1996 m, 1932 vs and 1876 s(sh) cm^{-1} indicating that all the

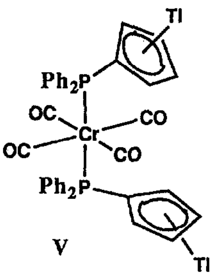
CO groups are terminal carbonyl groups. The $^{31}P\{^1H\}$ NMR spectrum of **III** exhibits a singlet at δ35.8 ppm. In addition to the phenyl proton resonances, the ^1H NMR spectrum of **III** also exhibits two multiplets of relative intensity 1 : 1 centred at δ6.31 and 5.96 ppm, respectively, for the protons of the cyclopentadienyl ring. This indicates that there are two sets of equivalent protons for the (C_5H_4Tl) ring. Based on the above spectroscopic data, the following structure is assigned to **III**.



III, M=Cr

IV, M=Mo

Unlike **III**, **V** is insoluble in most organic solvents. Thus, it is not possible to characterize **V** by NMR spectroscopy. The IR spectrum (KBr) of **V** exhibits only one absorption at 1876s cm^{-1}, indicating that the four carbonyl groups are terminal carbonyls having a *trans*-configuration. Thus, based on elemental analysis and IR data, the following structure is assigned to **V**.



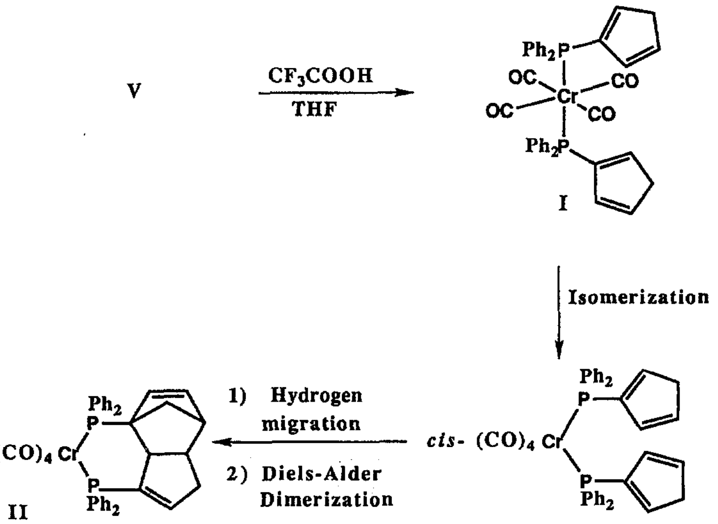
V

The proposed structure is further supported by the fact that when **V** was treated with CF_3CO_2H, **II** was isolated. Presumably upon protonation, **V** produces **I** which then isomerizes and undergoes Diels–Alder dimerization to give **II**, as shown in Scheme 2.

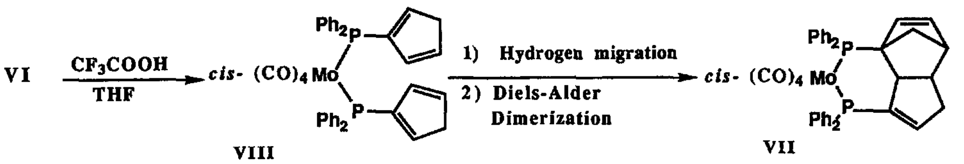
(2) When $C_7H_8Cr(CO)_4$ was treated with two equivalents of $Ph_2P(C_5H_4Tl)$ in THF, a greenish-yellow precipitate of stoichiometry $Cr(CO)_4[Ph_2P(C_5H_4Tl)]_2$ was isolated in 90% yield. The IR spectrum of the precipitate is identical to that of **V**. Thus, the interaction of $C_7H_8Cr(CO)_4$ with $Ph_2P(C_5H_4Tl)$ is a more convenient route for the preparation of **V**.

Preparation of $Mo(CO)_{6-n}[Ph_2P(C_5H_4Tl)]_n$ *complexes* (n = 1, 2)

(1) When $Mo(CO)_6$ was treated with one equivalent of trimethylamine N-oxide in THF followed by the addition of one equivalent of $Ph_2P(C_5H_4Tl)$, compounds of stoichiometry $Mo(CO)_5[Ph_2P(C_5H_4Tl)]$ (**IV**) and $Mo(CO)_4[Ph_2P(C_5H_4Tl)]_2$ (**VI**) were isolated in 65 and 12% yields, respectively. Compound **IV** is insoluble in hexane, but soluble in benzene, toluene, diethyl ether, THF, $CHCl_3$ and CH_2Cl_2. However, it slowly decomposes in $CHCl_3$ and CH_2Cl_2. The IR spectrum (KBr) of **IV** exhibits CO absorptions at 2065s, 1979s, and 1939 vs cm^{-1} indicating that all the CO groups are terminal carbonyl groups. The $^{31}P\{^1H\}$ NMR spectrum of **IV** exhibits a singlet at δ16.7 ppm. In addition to the phenyl proton resonances, the ^1H NMR spectrum of **IV** also exhibits two multiplets of relative intensity 1 : 1 centred at δ6.27 and 5.97 ppm, respectively,



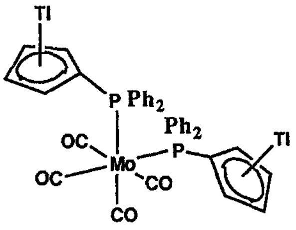
Scheme 2.



Scheme 3.

for the protons of the cyclopentadienyl ring. The spectroscopic data suggest that **IV** has the same structure as **III**.

Compound **VI** is insoluble in most organic solvents and thus, cannot be characterized by NMR spectroscopy. The IR spectrum (KBr) of **VI** exhibits CO absorptions at 2008 s, 1896 vs and 1896 s(sh) cm^{-1}, indicating that the four carbonyl groups are terminal carbonyls having the *cis*-configuration. Based on the above data, the following structure is assigned to **VI**.



VI

The proposed structure is further supported by the fact that when **VI** was treated with CF_3CO_2H, **VII** was isolated. Presumably upon protonation **VI** produces *cis*- $Mo(CO)_4[Ph_2P(C_5H_5)]_2$ (**VIII**), which then undergoes Diels–Alder dimerization to give **VII** as shown in Scheme 3.

In contrast to the chromium analogy which adopts a *trans*-configuration, **VI** adopts a *cis*-configuration. This observation can again be explained in terms of the difference in size between the two central atoms as was discussed previously.

(2) When $C_7H_8Mo(CO)_4$ was treated with two equivalents of $Ph_2P(C_5H_4Tl)$ in THF, an off-white precipitate of stoichiometry $Mo(CO)_4[Ph_2P(C_5H_4Tl)]_2$ was isolated in 90% yield. The IR spectrum of the precipitate is identical to that of **VI**. This shows that the interaction of $C_7H_8Mo(CO)_4$ with $Ph_2P(C_5H_4Tl)$ is a more convenient route for the preparation of **VI**. Compound **VI** can also be produced by the interaction of *cis*-$(CO)_4Mo[Ph_2P(C_5H_5)]_2$ (**VIII**) with two equivalents of Tl(OEt). When **VIII** was treated with two equivalents of Tl(OEt), an off-white precipitate was isolated and its IR spectrum was identical to that of **VI**.

CONCLUSION

We have synthesized *trans*-$Cr(CO)_4[Ph_2P(C_5H_5)]_2$ and demonstrated that coordinated $Ph_2P(C_5H_5)$ ligands are reluctant to undergo intermolecular dimerization. However, when two $Ph_2P(C_5H_5)$ ligands are in a mutually *cis*-position, the coordinated ligands will undergo a facile intramolecular Diels–Alder dimerization to produce the 1,3-bis(diphenylphosphino)dicyclopentadiene ligand. We have also prepared $M(CO)_5[Ph_2P(C_5H_4Tl)]$ and $M(CO)_4[Ph_2P(C_5H_4Tl)]_2$ complexes (M = Cr, Mo) which are potential synthetic reagents for the preparation of heterometallic complexes containing the $M(CO)_n$ (M = Cr, Mo ; $n = 4, 5$) unit. We are in the process of evaluating the potential of these complexes as heterometallic synthetic reagents. The results will be reported in a separate paper.

EXPERIMENTAL

Microanalyses were performed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, China. IR spectra (KBr pellets) were recorded on a Hitachi 270-30 IR spectrometer or on a Digilab FTS45 Fourier-transform IR spectrometer; data are given in cm^{-1}. NMR spectra were recorded on a JEOL FX90Q spectrometer. Chemical shifts of ^1H NMR spectra were referenced to internal deuterated solvents and then recalculated to TMS = $\delta 0.0$ ppm. ^{31}P NMR spectra were referenced to external 85% H_3PO_4.

All operations were carried out under nitrogen or *in vacuo*. All chemicals used were of reagent grade. Solvents were dried by standard procedures, distilled and deaerated prior to use. Melting points were taken in sealed capillaries and are uncorrected. $C_7H_8Cr(CO)_4$,[6] $C_7H_8Mo(CO)_4$,[6] $(C_5H_5)Tl$,[7] $Ph_2P(C_5H_5)$,[8] $Ph_2P(C_5H_4Tl)$[7] and *cis*-$Mo(CO)_4[Ph_2P(C_5H_5)]_2$[2] were prepared according to literature methods. *Trans*-$Cr(CO)_4(Ph_2PCl)_2$ was prepared by the interaction of $C_7H_8Cr(CO)_4$ with two equivalents of Ph_2PCl in refluxed hexane in 90% yield as a yellow crystalline solid. ^1H and $^{31}P\{^1H\}$ NMR data are given in Table 1.

Table 1. ^1H and $^{31}P\{^1H\}$ NMR data

Compound	^1H[a]	Assignment	^{31}P[b]	Assignment
I	7.40 m(20)	*Ph*$_2$P	20.0 s	Ph$_2$*P*(C_5H_5)
	6.84 m(2) 6.49 br, s(4)	Olefinic protons of the C_5H_5 rings		
	3.20 br, s(4)	Aliphatic protons of the C_5H_5 rings		
II	7.00–7.55 m(20)	*Ph*$_2$P	56.1 d(1)	P_a; J(P—P) = 34.2 Hz
	6.74 m(1) 6.12 m(1) 5.13 m(1)	Olefinic protons of the dicyclopentadiene liquid	41.0 d(1)	P_b; J(P—P) = 34.2 Hz
	1.62–2.87 m(6) 0.63 m(1)	Aliphatic protons of the dicyclopentadiene liquid		
III[c]	7.53 m(4) 7.16 m(6)	*Ph*$_2$PC$_5$H$_4$Tl	35.8 s	Ph$_2$*P*C$_5$H$_4$Tl
	6.31 m(2) 5.96 m(2)	Ph$_2$C$_5$*H*$_4$Tl		
IV[c]	7.50 m(4) 6.96 m(6)	*Ph*$_2$PC$_5$H$_4$Tl	16.7 s	Ph$_2$*P*C$_5$H$_4$Tl
	6.27 m(2) 5.97 m(2)	Ph$_2$PC$_5$*H*$_4$Tl		

[a] In $CDCl_3$ at 30°C, referenced to Me_4Si (δ0.00).

[b] In $CDCl_3$ at 30°C, referenced to external 85% H_3PO_4 (δ0.00), negative for upfield shift.

[c] In C_6D_6 at 30°C.

Abbreviations: s, singlet; d, doublet; m, multiplet; br, broad.

Preparation of trans-$Cr(CO)_4[Ph_2P(C_5H_5)]_2$ (I)

A solution of $C_7H_8Cr(CO)_4$ (0.35 g, 1.36 mmol) in hexane (25 cm^3) was added dropwise to a freshly prepared solution of $Ph_2P(C_5H_5)$ (0.75 g, 3 mmol) in hexane (25 cm^3) at 0°C. After stirring at 0°C for 2 h, the solution was filtered. The filtrate was concentrated to *ca* 20 cm^3 and cooled to −20°C to give a yellow crystalline solid, which was filtered and dried *in vacuo*. Yield: 0.72 g, 80%; m.p. 141–145°C (decomposed). Found (required): C, 68.2 (68.7); H, 4.5 (4.6)%. IR (KBr), ν(CO): 1880 s cm^{-1}.

Preparation of cis-$Cr(CO)_4(Ph_2PC_{10}H_{10}PPh_2)$ (II)

(1) A solution of **I** (0.66 g, 1 mmol) in toluene (25 cm^3) was stirred at room temperature. The reaction was monitored by IR and was stopped when the CO absorption peak due to **I** disappeared. The solution was then filtered and the solvent of the filtrate was removed *in vacuo*. A pale green residue was obtained which was dissolved in a minimum amount of CH_2Cl_2. Hexane was then added to the CH_2Cl_2 solution until it turned cloudy. The CH_2Cl_2/hexane solution was then cooled to −20°C to give light green crystals, which were filtered and dried *in vacuo*. Yield: 0.60 g, 90%; m.p. 200°C (decomposed). Found (required): C, 68.6 (68.7); H, 4.8(4.6)%. IR (KBr), ν(CO); 2002 s, 1912 s, 1872 vs(br) cm^{-1}.

(2) A solution of *trans*-$Cr(CO)_4(Ph_2PCl)_2$ (1.0 g, 1.65 mmol) in toluene (30 cm^3) was added dropwise to a suspension of $(C_5H_5)Tl$ (1.0 g, 3.72 mmol) in toluene (70 cm^3). The reaction mixture was refluxed for 16 h and filtered. The filtrate was evaporated to dryness *in vacuo* to give a green residue. The residue was redissolved in a minimum amount of CH_2Cl_2 and chromatographed on silica gel using CH_2Cl_2 as eluent. The green band obtained was concentrated to *ca* 15 cm^3 and then hexane was added until the solution turned cloudy. The CH_2Cl_2/hexane mixture was then cooled to −20°C to give green crystals of **II**. Yield: 0.93 g, 85%.

Preparation of $Cr(CO)_5[Ph_2P(C_5H_4Tl)]$ (III)

A solution of trimethylamine N-oxide (0.15 g, 2 mmol) in THF (10 cm^3) was added dropwise to a solution of $Cr(CO)_6$ (0.44 g, 2 mmol) in THF (20 cm^3). After stirring overnight at ambient temperature, a yellow solution was obtained which was filtered into a suspension of $Ph_2P(C_5H_4Tl)$ (0.9 g, 2 mmol) in THF (20 cm^3). The reaction mixture was allowed to stir at ambient temperature for 5 h before the solvent was removed *in vacuo* to give a greenish-yellow residue. The residue was extracted with diethyl ether (3 × 20 cm^3) to give a greenish-yellow solution and a greenish residue. The ether solution was then concentrated to *ca* 20 cm^3 and cooled to −20°C to give greenish yellow crystals which were filtered and dried *in vacuo*. Yield: 0.78 g, 60%; m.p. 178–180°C (decomposed). Found (required): C, 41.3 (40.9); H, 2.2(2.2)%. IR (KBr), ν(CO): 2060 m, 1996 m, 1932 vs, 1876 s(sh) cm^{-1}.

The greenish residue was insoluble in most organic solvents. The IR spectrum of the residue exhibited a strong CO absorption at 1856 cm^{-1} and was identical to that of *trans*-$Cr(CO)_4[Ph_2(C_5H_4Tl)]_2$ (**V**). Yield: 0.21 g, 10%.

Preparation of $Mo(CO)_5[Ph_2P(C_5H_4Tl)]$ (**IV**)

A solution of trimethylamine N-oxide (0.30 g, 4 mmol) in THF (10 cm^3) was added dropwise to a solution of $Mo(CO)_6$ (1.08 g, 4.1 mmol) in THF (30 cm^3). After stirring overnight at ambient temperature, a yellow solution was obtained which was then filtered into a suspension of $Ph_2P(C_5H_4Tl)$ (1.81 g, 4 mmol) in THF (20 cm^3). The reaction mixture was allowed to stir at ambient temperature for an additional 5 h to give a light yellow solution. The solvent of the reaction mixture was then removed *in vacuo* to give an off-white residue. The residue was extracted with diethyl ether (3 × 20 cm^3) to give a light yellow solution and an off-white solid. The ether solution was filtered, concentrated to *ca* 20 cm^3 and cooled to −20°C to give a white crystalline solid, which was filtered and dried *in vacuo*. Yield: 1.79 g, 65%; m.p. 130°C (decomposed). Found (required): C, 38.1(38.3); H, 2.0(2.2)%. IR (KBr), ν(CO): 2065 s, 1979 s, 1939 vs cm^{-1}. Compound **IV** is insoluble in saturated hydrocarbons, but soluble in benzene, toluene, diethyl ether, THF, $CHCl_3$ and CH_2Cl_2 and slowly decomposes in $CHCl_3$ and CH_2Cl_2. The off-white residue was insoluble in most organic solvents. The IR spectrum in KBr exhibited CO absorption at 2008 s, 1896 vs, 1860 s(sh) cm^{-1}, and is identical to that of **VI**. Yield: 0.53 g, 12%.

Preparation of trans-$Cr(CO)_4[Ph_2P(C_5H_4Tl)]_2$ (**V**)

(1) A solution of Tl(OEt) (0.25 g, 1 mmol) in toluene (5 cm^3) was added dropwise to a solution of *trans*-$Cr(CO)_4[Ph_2P(C_5H_5)]_2$ (**III**) (0.33 g, 0.5 mmol) in THF (20 cm^3) at ambient temperature. A greenish-yellow precipitate was obtained. The reaction mixture was allowed to stir for 2 h and then filtered. The greenish-yellow precipitate was then washed with THF (2 × 20 cm^3) and dried *in vacuo*. Yield of **V**: 0.48 g, 90%; m.p. 180°C (decomposed). Found (required): C, 42.4 (42.6); H, 2.4 (2.6)%. IR (KBr), ν(CO): 1876 s cm^{-1}. The complex was too insoluble for characterization by NMR, but addition of CF_3CO_2H to a suspension of the complex in THF at ambient temperature gave **II** in quantitative yield.

(2) A solution of $C_7H_8Cr(CO)_4$ (0.51 g, 2 mmol) in THF (20 cm^3) was added dropwise to a suspension of $Ph_2P(C_5H_4Tl)$ (1.81 g, 4 mmol) in THF (20 cm^3) at ambient temperature. The reaction mixture was allowed to stir overnight at ambient temperature. A greenish yellow precipitate was obtained and the solution was filtered. The greenish-yellow precipitate was then washed with THF (2 × 20 cm^3) and dried *in vacuo*. The IR spectrum of the precipitate was identical to that of **V**. Yield: 1.92 g, 90%.

Preparation of cis-$Mo(CO)_4[Ph_2P(C_5H_4Tl)]_2$ (**VI**)

(1) A solution of Tl(OEt) (0.50 g, 2 mmol) in toluene (10 cm^3) was added dropwise to a solution of *cis*-$Mo(CO)_4[Ph_2P(C_5H_5)]_2$ (0.71 g, 1 mmol) in THF (20 cm^3) at ambient temperature. An off-white precipitate was obtained. The reaction mixture was allowed to stir for 2 h and then filtered. The off-white precipitate was then washed with THF (2 × 20 cm^3) and dried *in vacuo*. Yield of **VI**: 1.00 g, 90%; m.p. 130°C (decomposed). Found (required): C, 40.4(40.9); H, 2.4(2.5)%. IR (KBr), ν(CO): 2008 s, 1896 vs, 1860 s(sh) cm^{-1}. The complex was too insoluble for characterization by NMR, but addition of CF_3CO_2H to a suspension of the complex in THF at ambient temperature gave *cis*-$Mo(CO)_4(Ph_2PC_{10}H_{10}PPh_2)$ in quantitative yield.

(2) A solution of $C_7H_8Mo(CO)_4$ (0.60 g, 2 mmol) in THF (20 cm^3) was added dropwise to a suspension of $Ph_2P(C_5H_4Tl)$ (1.81 g, 4 mmol) in THF (20 cm^3) at ambient temperature. The reaction mixture was allowed to stir overnight at ambient temperature. An off-white precipitate was obtained and the solution was filtered. The precipitate was washed with THF (2 × 20 cm^3) and dried *in vacuo*. Yield: 1.89 g, 85%. The IR spectrum of the precipitate was identical to that of **VI**. Addition of excess CF_3CO_2H to a suspension of the precipitate in THF gave *cis*-$Mo(CO)_4(Ph_2PC_{10}H_{10}PPh_2)$ in quantitative yield.

$^{31}P\{^1H\}$ *NMR study on the isomerization of* **I** *to* **II**

Compound **I** (20 mg) was dissolved in $CDCl_3$ (0.5 cm^3) at 30°C. The isomerization process was monitored by $^{31}P\{^1H\}$ NMR spectroscopy at 4 h intervals for 12 h. Within the period, **I** isomerized to **II** quantitatively. Throughout the course of the reaction, other than those of **I** and **II**, no other resonance signals were observed.

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REFERENCES

1. G. K. Anderson and M. Lin, *Organometallics* 1988, **7**, 2285 and refs therein.
2. W. K. Wong, F. L. Chow, H. Chen, R.-J. Wang and T. C. W. Mak, *Polyhedron* 1990, **9**, 2469.
3. G. G. Garvin, T. J. Sloan and R. J. Puddephatt, *Polyhedron* 1987, **6**, 1797.
4. D. T. Thompson, British Patent, 1,156,336 (C1.C075), 25 June 1969, Appl. 2 August 1966–2 March 1967; 4 pp.
5. W. K. Wong, F. L. Chow, H. Chen and T. C. W. Mak, *J. Organomet. Chem.* 1989, **377**, C65.
6. J. J. Eisch and R. B. King, *Organometallic Synthesis*, Vol. 1, pp. 124–125. Academic Press, New York (1965).
7. G. K. Anderson and M. Lin, *Organometallics* 1988, **7**, 2285.
8. F. Mathey and J. P. Lampin, *Tetrahedron* 1975, **31**, 2685.