

Note

Synthesis and characterization of chromium and molybdenum(0) complexes bearing the (pentafluoroethyl)diphenylphosphine (pfpep) ligand

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Abstract

The synthesis and characterization of two Group VI pentacarbonyl complexes (pfpep)M(CO)₅ (M = Cr **1**, Mo **2**; pfpep = PPh₂C₂F₅) are reported. Thermolysis of M(CO)₆ and pfpep in refluxing octane afforded **1** and **2** in moderate yields. These complexes were completely characterized by multinuclear NMR, IR and elemental analysis. X-ray structures for these complexes indicated they were isostructural, crystallizing in triclinic unit cells with four molecules per asymmetric unit. A comparison of the bond lengths in **1** and **2** to other (L)M(CO)₅ complexes showed a relationship between the M–C_{ax} bond length and the electronic influence of the phosphine ligand, and establishes the pfpep ligand as neither electron-rich nor electron-poor. A comparison of IR data with other (L)M(CO)₅ complexes also indicates the pfpep ligand is electronically neutral, with an electronic influence that approximates phosphites.

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1. Introduction

Tertiary phosphines, PR₃, are among the most utilized group of ligands in transition metal chemistry, due to the ease with which the steric and electronic properties of phosphine ligands are controlled [1]. Many of the structure/reactivity relationships involving phosphines have focused on the introduction of traditional hydrocarbon substituents to the phosphorus atom. Phosphine ligands bearing hydrocarbon groups tend to be viewed as electron rich, and the development of electroneutral or electron-poor phosphines has not kept

pace. An a priori assessment of the stereoelectronic profile of known phosphine ligands indicated several large voids, which include large, electron-poor phosphines and electronically moderate phosphines (neither electron-rich nor electron-poor), which confirms that development of electronically neutral and/or electron poor phosphines lags that of electron rich phosphines [2]. Given the ubiquitous nature of phosphines in organometallic chemistry and the incredible number of reactions catalyzed by metal–phosphine complexes, these voids are quite noteworthy in that they represent an opportunity of phosphine ligand development and the potential for discovery of novel reaction pathways.

With this consideration in mind, research in our group has focused on the development of a new class of phosphines of the type R₂PR_f, (R = hydrocarbon

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substituent; $R_f = C_2F_3$ or C_2F_5). Phosphine ligands bearing fluoroalkyl and fluorovinyl groups are readily prepared via treatment of R_fLi with an appropriate P–Cl precursor [3–6]. We have already reported some of our preliminary studies of Group VI hexacarbonyl substitution chemistry [7,8]. We have most recently reported the synthesis and characterization of pentafluoroethylidene-phenylphosphine (pfepp), prepared by treatment of Ph_2P-Cl with C_2F_5Li , and its coordination chemistry with platinum [9,10].

The present work is part of a continuing effort to prepare and characterize electroneutral phosphine ligands. In an effort to more broadly establish the electronic influence of the pfepp ligand, we now wish to report some of the substitution chemistry of Group VI hexacarbonyl complexes with pfepp. Treatment of $M(CO)_6$ with one equivalent of pfepp in refluxing octane yielded the desired pentacarbonyl complexes, $M(CO)_5(pfepp)$ ($M = Mo, Cr$). IR and X-ray crystal structure data of these complexes support the conclusion that the pfepp ligand approximates the electronic influence of phosphites.

2. Experimental

2.1. General considerations

All manipulations were conducted under an inert atmosphere using glove box, high-vacuum and/or Schlenck techniques. Water and oxygen free solvents were prepared from sodium/benzophenone and vacuum distilled prior to use. Metal hexacarbonyl starting materials were obtained from Aldrich and used without further purification. 1H , ^{19}F and ^{31}P NMR spectra were measured using a JEOL 270 MHz spectrometer operating at 270.17, 254.21 and 109.37 MHz, respectively. ^{31}P and ^{19}F NMR spectra were externally referenced to H_3PO_4 and $CFCl_3$, respectively, with downfield shifts taken to be positive. Infrared spectra were obtained on a Perkin–Elmer FTIR instrument as Nujol mulls. Elemental analyses were obtained from Desert Analytics. $PPh(C_2F_5)_2$ was prepared as described previously [9].

2.2. $Cr(CO)_5(pfepp)$

$Cr(CO)_6$ (0.320 g, 1.45 mmol) and 15 ml of octane were combined in a 25 ml flask fitted with a reflux condenser and attached to a nitrogen manifold. To this solution was added 0.459 g (1.51 mmol) of pfepp and the solution was refluxed under nitrogen for 18 h. The solution was transferred to a filtration assembly for workup. The octane was removed under vacuum, the residue was slurried in diethyl ether and filtered, removing traces of black residue assumed to be $Cr(0)$ or Cr oxides. Removal of ether followed by the addition of 2

ml of hexane and cooling to -78 °C yielded 0.471 g (65.2%) of $Cr(CO)_5(Ph_2PC_2F_5)$ as a yellow solid. Anal. Calc. for $C_{19}H_{10}F_5O_5PCr$: C, 45.99; H, 2.03. Found: C, 45.86; H, 1.95%. 1H NMR (C_6D_6): δ 7.55 (m, 2H), 6.92 (m, 3H). ^{19}F NMR ($CDCl_3$): δ -76.5 (s, CF_3); -108.5 (d, $^2J_{PF} = 62$ Hz, CF_2). ^{31}P NMR (C_6D_6): δ 80.77 (t, $^2J_{PF} = 62$ Hz, $P-CF_2$). IR (nujol, cm^{-1}): 2072 (s), 1995 (m), 1954 (s), 1300 (m), 1218 (s), 1115 (m), 960 (m).

2.3. $Mo(CO)_5(pfepp)$

The procedure for this synthesis is analogous to the Cr Complex except the reflux time was shortened to 5 h. Workup and isolation as before afforded 0.391 g (48.2%) of $Mo(CO)_5(pfepp)$ as a white/light gray solid. Anal. Calc. for $C_{19}H_{10}F_5O_5PMo$: C, 42.25; H, 1.86. Found: C, 41.93; H, 2.10%. 1H NMR (C_6D_6): δ 7.55 (m, 2H); 6.94 (m, 3H). ^{19}F NMR ($CDCl_3$): δ -76.5 (s, CF_3); -109.5 (d, $^2J_{PF} = 65$ Hz, CF_2). ^{31}P NMR (C_6D_6): δ 58.8 (t, $^2J_{PF} = 65$ Hz, $P-CF_2$). IR (nujol, cm^{-1}): 2080 (s), 2000 (m), 1960 (s), 1300 (m), 1208 (s), 1115 (m), 960 (m).

2.4. X-ray diffraction studies

The crystallographic data for compounds **1** and **2** are summarized in Table 2. Crystals of compound **1** were isolated from an overnight room temperature evaporation of a 1:1 mixture of diethyl ether and pet ether. Crystals of **2** were obtained from a slow evaporation of a petroleum ether solution. Single crystal X-ray data for **1** and **2** were collected on a Bruker P4 diffractometer equipped with a molybdenum tube ($\lambda = 0.71073$ Å) and a graphite monochromator. Empirical absorption corrections based on face indexing and integration were applied; the structures were solved by direct methods and refined by full matrix least squares techniques on F^2 using structure solution programs from the BRUKER/SHELX 97 system. All nonhydrogen atoms were refined anisotropically, while hydrogen atoms were placed in calculated positions and refined with fixed isotropic thermal parameters. Crystallographic data for the structural analysis of **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 247993 for **1** and CCDC No. 247994 for **2**.

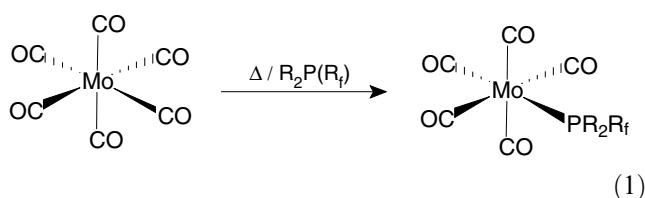
3. Results and discussion

Thermolysis of $M(CO)_6$ with one equivalent of pfepp in refluxing octane yielded the monosubstituted pentacarbonyl complexes $M(CO)_5(pfepp)$ ($M = Cr$ **1** and Mo **2**) as seen in Eq. (1). $Cr(CO)_5(pfepp)$ was isolated in moderate yield (65%) as a yellow solid after an ether extraction from decomposed starting material followed

Table 1
A₁⁽²⁾ IR (cm⁻¹) frequency data for Mo(CO)₅ (L) complexes

Ligand (L)	Mo(CO) ₅ (L)
PMe ₃	2071 [13]
PPh ₃	2073 [13]
PPh ₂ (CF=CF ₂)	2078 [15]
P(OEt ₃) ₃	2078 [15]
Ph ₂ PC ₂ F ₅	2080
P(OPh) ₃	2083 [15]
PBr ₃	2093 [15]
PCl ₃	2095 [15]

by isolation from hexane at -78 °C. Similar workup of the molybdenum analog yielded Mo(CO)₅(pfepp) as a white/tan solid, again in moderate yield (49%).



The presence of several spin active nuclei allowed these complexes to be readily characterized by multinuclear NMR. ³¹P NMR for **1** showed a single resonance at 82.2 ppm, a significant downfield shift from the free ligand peak (-1.4 ppm) [9]. The ²J_{PF} of 62 Hz for **1** was similar to the free ligand peak (58 Hz), though the ³J_{PF} for **1** dropped to ~0 Hz (³J_{PF} for pfepp = 16.5 Hz). ³¹P NMR for **2** also showed a single resonance at

59 ppm and a similar ²J_{PF} of 65 Hz and no ³J_{PF} coupling. ¹⁹F data were relatively insensitive to the metal center, as both complexes showed peaks typical for CF₃ and CF₂ groups at -76 and -108 ppm, respectively.

A comparison of the IR CO stretching modes of these compounds can be used as a qualitative indicator of the relative electronic influence of these phosphines with the metal center. Compounds of the type (R₃P)M(CO)₅ possess pseudo C_{4v} symmetry and three IR active bands attributable to CO stretches. The A₁⁽²⁾ CO stretching mode is an easily identified band that varies in a consistent fashion, and depends on the relative donor ability of the phosphine ligand. Table 1 shows a comparison of IR stretching frequencies for a variety of (L)Mo(CO)₅ complexes and clearly establishes the electronic influence of the pfepp ligand approximates phosphites and the perfluorovinyl analog PPh₂(CF=CF₂).

X-ray quality crystals of both **1** and **2** were grown from the slow evaporation of a pentane or an ether/pet ether solution. The complexes are isomorphous, possessing triclinic crystal symmetry with four molecules per asymmetric unit (Z = 8) and an ORTEP drawing of **1** is shown in Fig. 1. The presence of 4 molecules per asymmetric unit was verified for **1** based on determination of identical lattice constants for three different crystals and the variations in torsional angles of the four conformers.

Bond length data from (L)M(CO)₅ complexes is often used as an indirect measure of the electronic character-

Table 2
Crystal data and structure refinement data for (CO)₅Cr[PPh₂(C₂F₅)] and (CO)₅Mo[PPh₂(C₂F₅)]

	(CO) ₅ Cr[PPh ₂ (C ₂ F ₅)]	(CO) ₅ Mo[PPh ₂ (C ₂ F ₅)]
Empirical formula	C19H10CrF5O5 P	C19H10F5O5MoP
Formula weight	496.24	540.18
Crystal system	Triclinic	Triclinic
Space group	P $\bar{1}$	P $\bar{1}$
Unit cell dimensions		
<i>a</i> (Å)	12.0861(6)	12.1674(9)
<i>b</i> (Å)	12.2000(6)	12.2604(12)
<i>c</i> (Å)	28.382(2)	28.918(3)
α (°)	92.676(4)	92.837(5)
β (°)	93.598(4)	93.588(6)
γ (°)	90.493(4)	90.527(5)
Volume (Å ³)	4171.9(4)	4299.9(7)
Z	8	8
D _{calc} (Mg/m ³)	1.580	1.669
Absorption coefficient (mm ⁻¹)	0.697	0.754
F(000)	1984	2128
Crystal size (mm ³)	0.58 × 0.46 × 0.40	0.50 × 0.40 × 0.23
Theta range for data collection (°)	1.79–25.00	1.77–25.03
Reflections collected	16,882	17,430
Independent reflections (R _{int})	14,614 (0.0224)	15,069 (0.0236)
Maximum and minimum transmission	0.780 and 0.702	0.861 and 0.749
Temperature (K)	293(2)	293(2)
Data/restraints/parameters	14,614/0/1117	15,069/0/1117
Final R indices [I > 2σ(I)]	R ₁ = 0.0392, wR ₂ = 0.0986	R ₁ = 0.0370, wR ₂ = 0.0957
R indices (all data)	R ₁ = 0.0607, wR ₂ = 0.1087	R ₁ = 0.0532, wR ₂ = 0.1185

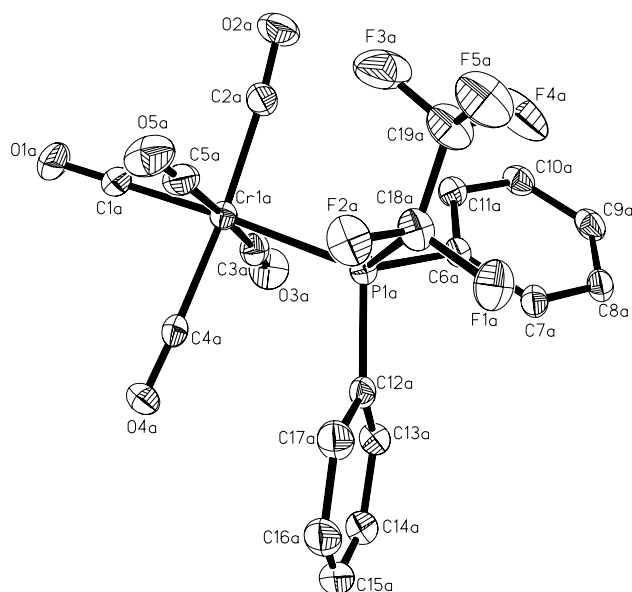


Fig. 1. ORTEP drawing of (pfpep)Cr(CO)₅. Hydrogen atoms have been omitted for clarity. Selected bond length (Å) and angle (°) data for **1** and **2**: (pfpep)Cr(CO)₅ **1**, Cr–P(1) 2.3663(9), Cr–C(1)_{axial} 1.870(4), Cr–C(eq)_{av} 1.903(4), C(1)–Cr–P(1) 176.14(11). (pfpep)Mo(CO)₅ **2**, Mo–P(1) 2.5106(11), Mo–C(1)_{axial} 2.012(5), Mo–C(eq)_{av} 2.049(5), C(1)–Mo–P(1) 174.83(14).

istics of a phosphine ligand. The Cr–P bond distance in **1** of is 2.3663(9) Å and the Mo–P bond length of **2** is 2.5016(11) Å. The Cr–P bond length of (pfpep)Cr(CO)₅ is essentially identical to the Cr–P bond length of 2.3664(5) Å in (PMe₃)Cr(CO)₅ [11] and is only slightly shorter than the Cr–P bond of 2.422(1) Å in the PPh₃ analog [12,13]. Similar comparisons between the Mo–P bond distances in **2** and other (L)Mo(CO)₅ complexes indicates there is little correlation between the electronic influence of a phosphine ligand and the metal–phosphorus bond. The Mo–P bond length of **2** is 2.5016(11) Å is again almost identical to the Mo–P bond distance of several (L)Mo(CO)₅ complexes [L = PMe₃ (2.5082 Å) [11], P(CH₂CH₂CN)₃ (2.506 Å) [14], PPh₂(CF=CF₂) (2.5168 Å) [7] bearing phosphines with varying electronic characteristics.

The equatorial metal carbonyl bonds are also relatively insensitive to the electronic nature of the phosphine ligand. The average M–C_{eq} for (PF₃)Mo(CO)₅ is 2.045 Å [12] and the average bond length for the (PMe₃)Mo(CO)₅ analog is 2.036 Å [11]. Similar comparisons for the chromium complexes also show no dependence of the M–C_{eq} bond length with the phosphine ligand. The average M–C_{eq} for (PF₃)Cr(CO)₅ is 1.886 Å [12] and the bond length for the (PMe₃)Mo(CO)₅ analog is 1.850(2) Å [11]. The average M–C_{eq} bond length in the pfpep derivatives is 1.903 Å for **1** and 2.049 Å for **2**.

While the metrical data from M–P and M–C_{eq} bond distances for (L)M(CO)₅ complexes is independent of

Table 3
M–C_{ax} bond distance data (Å) for (L)M(CO)₅ complexes

Ligand (L)	(L)Cr(CO) ₅	(L)Mo(CO) ₅
PMe ₃	1.850(2) [11]	1.984(4) [11]
PPh ₃	1.845(4) [16,17]	1.995(3) [14]
PPh ₂ (CF=CF ₂)	N/A	1.996(4) [7]
P(OPh) ₃	1.861(4) [16]	N/A
Ph ₂ PC ₂ F ₅	1.870(4)	2.012(5)
PCl ₃	1.900(4) [11]	2.035(2) [12]
PF ₃ (calc'd) [12]	1.886	2.045

the electronic impact of the bound phosphine ligand, the M–C_{ax} distance varies in a systematic fashion and is readily related to the electronic character of the ligand. The M–C_{ax} elongates as the phosphine ligand becomes more electron poor. This observation is readily rationalized; by reducing the electron density at the metal center the amount of electron density available for overlap into the π* orbital of the CO ligand *trans* to the phosphine is also reduced. The reduced overlap weakens the M–C bond, which slightly elongates the bond. Table 3 shows a list of M–C_{ax} bond distances for a number of (L)Mo(CO)₅ and (L)Cr(CO)₅ complexes. In both series, the longest bond belongs to the PCl₃ derivative (1.900(4) Å for (PCl₃)Cr(CO)₅ and 2.035(2) Å for (PCl₃)Mo(CO)₅) [11,12] and the shortest bond occurs in the PMe₃ derivative (1.850(2) and 1.984(4) for the Cr and Mo complexes, respectively) [11]. The M–C_{ax} bond length data for **1** and **2** (1.870(4) Å for **1** and 2.012(5) Å for **2**) clearly show the electronic influence of the pfpep ligand approximates phosphites and PPh₂(CF=CF₂).

The metal centers of **1** and **2** sit in the center of a slightly distorted octahedron. The four equatorial carbonyls are planar but the metal center lies out of this plane, puckered slightly towards the phosphorus ligand. Consequently, all four C_{ax}–M–C_{eq} bonds are slightly less than 90°. The P–M–C_{ax} bond angle of 176.14° is slightly deflected from the idealized 180°. This deflection of the M–P bond results in P–M–C₃ (and C₄) bond angles that are slightly less than 90° and P–M–C₂ (and C₅) bond angles that are slightly greater than 90°.

4. Conclusions

Two new Group VI pentacarbonyl complexes (pfpep)M(CO)₅ (M = Cr **1**, Mo **2**; pfpep = PPh₂C₂F₅) were prepared and characterized by IR, NMR, EA and X-ray crystallography. A comparison of IR stretching frequencies and M–C_{ax} bond length data with other (L)M(CO)₅ complexes indicates the pfpep ligand is an electroneutral phosphine, with an electronic influence that approximates phosphites. The pfpep ligand occupies one of the two voids in the stereoelectronic profile of typical phosphine ligands.

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