Substituted Metal Carbonyls. Part 21.[1] $[\mathrm{M(CO)_5(dppf}\text{-}P)]$ $[\mathrm{M = Cr, Mo\ or\ W;\ dppf = Fe(C_5H_4PPh_2)_2}]$ as a Metalloligand in Heteropolymetallic Aggregates of $\mathrm{Au^{I}}$, $\mathrm{Pd^{II}}$ and $\mathrm{Pt^{II}}$. Crystal and Molecular Structures of $[\mathrm{PtCl_2\{(\mu\text{-}dppf)W(CO)_5\}_2}]$ and $[\mathrm{Mo(CO)_5(dppf}\text{-}P)]$

Lai-Tee Phang,[a] Steve C. F. Au-Yeung,[b] T. S. Andy Hor,[a] Soo Beng Khoo,[a] Zhong-Yuan Zhou[b] and Thomas C. W. Mak[b]

[a] *Department of Chemistry, Faculty of Science, National University of Singapore, Kent Ridge 0511, Singapore*

[b] *Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong*

The complexes $[\mathrm{M(CO)_5(dppf}\text{-}P)]$ [M = Cr, Mo or W; dppf = 1,1′-bis(diphenylphosphino)ferrocene] behave like a monodentate phosphine ligand and displace the labile ligands from $[\mathrm{AuCl(SMe_2)}]$, *trans*-$[\mathrm{PdCl_2(PhCN)_2}]$ and *cis*-$[\mathrm{PtCl_2(dmso)_2}]$ (dmso = dimethyl sulfoxide) to yield the corresponding dppf-bridged heteropolymetallic complexes of general formula $[\mathrm{M'Cl_x\{(\mu\text{-}dppf)M(CO)_5\}_y}]$ (M′ = Au, $x = y = 1$; M′ = Pd or Pt, $x = y = 2$). Only the *trans* isomers have been isolated for $\mathrm{Pd^{II}}$ and $\mathrm{Pt^{II}}$. Isomerisation of the M′ = Pt, M = Cr complex to the *cis* form, followed by partial elimination of $[\mathrm{Cr_2(CO)_{10}(\mu\text{-}dppf)}]$ to form $[\mathrm{PtCl_2(dppf}\text{-}P,P')]$, after 3 d in $\mathrm{CDCl_3}$ was revealed by NMR spectroscopy. The solution characteristics of both geometrical isomers of the representative M′ = Pt, M = Cr complex have been established by two-dimensional NMR studies. UV-Photolytic degradation of the M′ = Pd or Pt, M complexes generally gave $[\mathrm{M(CO)_6}]$, $[\mathrm{M(CO)_4(dppf}\text{-}P,P')]$, $[\mathrm{M_2(CO)_{10}(\mu\text{-}dppf)}]$ and $[\mathrm{M'Cl_2(dppf)}]$. The molecular structures of *trans*-$[\mathrm{PtCl_2\{(\mu\text{-}dppf)W(CO)_5\}_2}]$ and $[\mathrm{Mo(CO)_5(dppf}\text{-}P)]$ have been determined. The former represents a trimetallic pentanuclear aggregate and the latter a metalloligand with a pendant phosphine on a bimetallic complex. Cyclic voltammetry of all the complexes has been examined and generally reveals one chemically reversible phosphinoferrocene-based oxidation, followed by an irreversible oxidation of the complex.

The ligating ability of 1,1′-bis(diphenylphosphino)ferrocene (dppf) is well documented.[2] Its complexes $[\mathrm{M(CO)_5(dppf)}]$ (M = Cr, Mo or W) also possess a pendant phosphine which confers upon it the capacity for further co-ordination. This heterometalloligand provides a facile and systematic entry into heteropolynuclear aggregates, as described herein. A similar approach has been reported for other complexes of mono-co-ordinated diphosphines which contain a hydrocarbon backbone.[3] Of special note is the report of a stable and isometrically pure *cis* form of a trinuclear complex $[\mathrm{PtCl_2\{(\mu\text{-}dppe)W(CO)_5\}_2}]$ (dppe = $\mathrm{Ph_2PCH_2CH_2PPh_2}$) isolated from a mixture of $[\mathrm{W(CO)_5(dppe}\text{-}P)]$ and $\mathrm{K_2[PtCl_4]}$.[3d]

The use of a ferrocene-based diphosphine offers a simple pathway into electroactive polymetallics. The electroactivity of dppf has been a subject of intense interest. In using it as a building block for higher aggregates with different metal atoms, we hope to explore the electroactivity of individual ferrocenyl sites and its effect on the overall redox behaviour of the complex. The flexibility in the tuning of the redox potential of the complex aggregate is also enhanced by changing the metals on either or both ends of the metalloligand dppf. In this paper we examine the effect of the metal carbonyl site for M = Cr, Mo and W, and vary the phosphine binding site between $\mathrm{Pd^{II}}$, $\mathrm{Pt^{II}}$ and $\mathrm{Au^{I}}$. The syntheses, NMR and cyclic voltammetric properties are presented and discussed. The solid-state structures of a representative parent metalloligand $[\mathrm{Mo(CO)_5(dppf}\text{-}P)]$ and polymetallic $[\mathrm{PtCl_2\{(\mu\text{-}dppf)W(CO)_5\}_2}]$ are also reported.

Results and Discussion

Complexation of $[\mathrm{M(CO)_5(dppf}\text{-}P)]$.—(*a*) *With* $[\mathrm{AuCl(SMe_2)}]$. The complexes $[\mathrm{AuCl\{(\mu\text{-}dppf)M(CO)_5\}}]$ are prepared by ligand substitution of $[\mathrm{AuCl(SMe_2)}]$ with $[\mathrm{M(CO)_5(dppf}\text{-}P)]$ and characterised by IR, ^{1}H and ^{31}P NMR spectroscopy, as well as elemental analyses (Table 1). Besides the peak assignable to the phosphorus bonded to the Group 6 metal,[4] the ^{31}P NMR spectra consist of a single peak at δ 28.26 due to the gold-co-ordinated phosphorus.

(*b*) *With trans*/*cis*-$[\mathrm{MCl_2(solv)_2}]$ (M = Pd, solv = PhCN; M = Pt, solv = dmso). Reactions of $\mathrm{K_2[MCl_4]}$, $\mathrm{MCl_2}$ or $[\mathrm{MCl_2(solv)_2}]$ (M = Pd or Pt; solv = MeCN, PhCN, *etc.*) with dppf invariably yield the corresponding chelates $[\mathrm{MCl_2(dppf)}]$ in its *cis* configuration.[5] However, similar reactions with $[\mathrm{M(CO)_5(dppf}\text{-}P)]$ which bears a pendant phosphine are less predictable for the latter serves as a monodentate ligand with a flexible backbone. The isomeric preference is a subject of our interest. Though the *cis* complexes are generally considered the thermodynamically stable forms, sterically demanding phosphines are known to favour the *trans* counterparts, and the coexistence of both isomers in solution has been noted.[6]

When $[\mathrm{M(CO)_5(dppf}\text{-}P)]$ was treated with *trans*-$[\mathrm{PdCl_2(PhCN)_2}]$, *trans*-$[\mathrm{PdCl_2\{(\mu\text{-}dppf)M(CO)_5\}_2}]$ was produced. Infrared data in the CO stretching region are as expected and the ^{31}P NMR spectra comprise signals due to the Group 6 metal-co-ordinated phosphine, together with a peak at δ 14.67 assigned to the co-ordination of phosphine to $\mathrm{Pd^{II}}$ (Table 1). In a representative ^{1}H NMR spectrum, three peaks in the region δ 4.23–5.07 are attributable to the cyclopentadienyl protons. Decoupling experiments suggest that the two lower-field signals

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

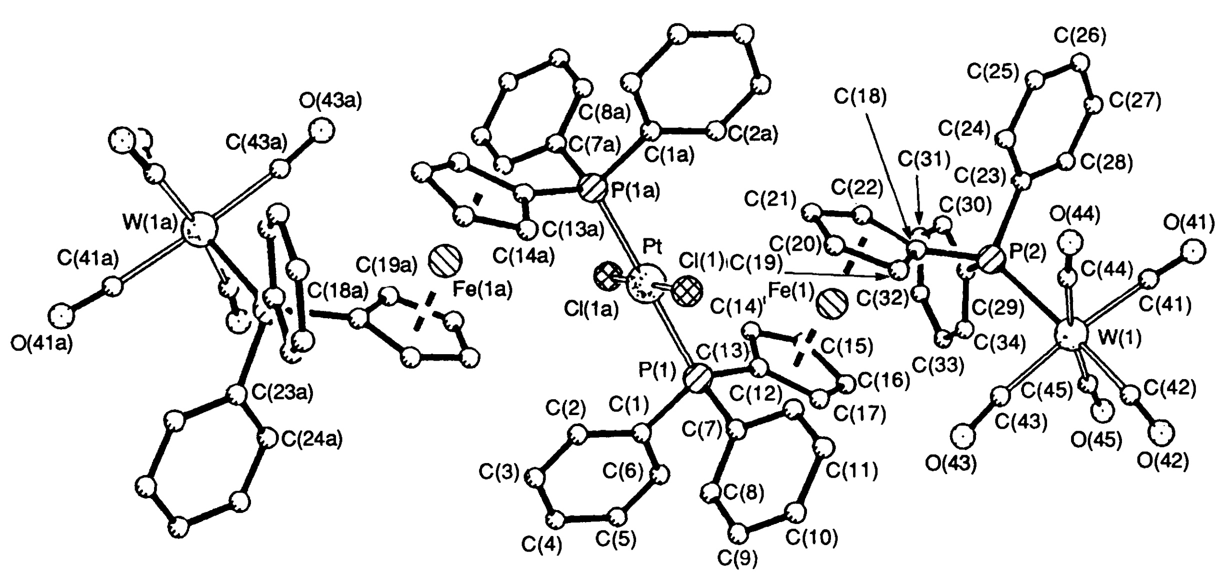

Fig. 1 Molecular structure of *trans*-$[PtCl_2\{(\mu\text{-dppf})W(CO)_5\}_2]$ showing the atomic labelling scheme

correspond to protons of C_5H_5 co-ordinated to palladium while the high-field broad singlet represents the remaining eight C_5H_4 protons.

In the reaction of $K_2[PtCl_4]$ or *cis*-$[PtCl_2(dmso)_2]$ (dmso = dimethyl sulfoxide) with $[M(CO)_5(dppf\text{-}P)]$ spectroscopic evidence showed that the *trans* isomer was produced with dmso displaced by two $M(CO)_5(dppf\text{-}P)$ metalloligands (Table 1). Besides the similar splitting patterns and chemical shifts of the proton signals to that of the palladium complex, in the ^{31}P NMR spectra the P–Pt coupling constants in the range 2630–2632 Hz for the complexes are significantly lower than that found in *cis*-$[PtCl_2\{(\mu\text{-dppe})W(CO)_5\}_2]$ (3642 Hz) and other *cis*-$PtCl_2L_2$ complexes which are in the region of 3600 Hz, and are consistent with the formation of the *trans* isomers.[6a,7] An X-ray single-crystal diffraction study was carried out on a representative complex, $[PtCl_2\{(dppf)W(CO)_5\}_2]$, in order to verify the solid-state structure of these complexes.

NMR and Solution Properties of trans-$[PtCl_2\{(dppf)Cr(CO)_5\}_2]$.—The solution integrity of this complex was examined in detail in $CDCl_3$ at room temperature because of its ease in purification and good yield. Assuming that the complex is isostructural to the Pt–W complex, the labelling scheme in Fig. 1 is adopted for the discussion below. Thus, Cp_1 is defined by the five-membered ring C(13)–C(17), Cp_2 from C(18)–C(22) [Cp_{1a} and Cp_{2a} are hence symmetry equivalents of Cp_1 and Cp_2 respectively] whereas φ_1 is defined by C(1)–C(6), φ_2 by C(7)–C(12) and φ_3 by the set of phenyl rings defined by C(23)–C(34). The ^1H NMR spectra of the *trans*-Pt–Cr complex was readily assigned. The ^1H–^1H decoupling and low-temperature experiments support the assignment of the peak at $\delta(^1H)$ 4.23 to $Cp_{2,2a}$.* The two peaks at $\delta(^1H)$ 5.07 and 4.33 are assigned to the H_β and H_α protons respectively on $Cp_{1,1a}$ based on combined correlation spectroscopy (COSY) as well as a ^1H–^1H decoupling experiment in which the former collapses to a singlet and the latter a doublet [$^3J(PH)$ = 1.71 Hz]. The *J*-resolved experiment resolved the multiplets on H_α and H_β [$\delta_H(Cp_{1,1a})$ 4.321 and 4.338 (J = 1.60), 5.063 and 5.080 (J = 1.60 Hz)]. Motional analysis allowed the assignment of the broad singlet in the phenyl region to $\varphi_{3,3a}$ whereas the other signals in the same region are all assigned to $\varphi_{1,1a}$ and $\varphi_{2,2a}$. The observed spectral information is summarised in Table 1.

After 3 d an isomerisation mixture containing the *trans* and *cis* complexes was detected together with small amounts of $[PtCl_2(dppf)]$ and $[Cr_2(CO)_{10}(\mu\text{-dppf})]$. The latter were decomposition products. Well defined spectral changes in both the ^{31}P as well as the ^1H NMR spectra were observed. The ^{31}P NMR spectrum recorded at 25 °C yields shifts and coupling constants consistent with those reported for both isomers of $[PtCl_2(PPh_{3-n}R_n)_2]$ (n = 1–3, R = Et, Pr or Bu).[6a] The small difference in the *cis* and *trans* shifts of 0.5 ppm indicates that the P(1)–Pt–P(1a) angle in the *cis* isomer is much larger than 90° and may well approach the *trans* angle due to the spatial demand of the $M(CO)_5(dppf)$ metalloligands. Steric relief is hence necessary in order to accompany the skeletal changes which take place about the platinum(II) centre. In the cyclopentadienyl proton region the new peaks at $\delta(^1H)$ 4.03 and 4.12 were assigned to H_β and H_α respectively on $Cp_{2,2a}$ for the *cis* complex, those at δ 4.17 and 4.33 to H_β and H_α respectively on $Cp_{1,1a}$. These latter peaks were overalapped by the H_α protons on $Cp_{2,2a}$ of the *cis* complex and H_α on $Cp_{1,1a}$ of the *trans* complex respectively. Aside from the obvious changes in the Cp region in the ^1H NMR spectra, the most notable change in the phenyl region is the small multiplet at $\delta(^1H)$ 7.075 upfield to the normal phenyl ring protons. The only possibility that could account for this result would be that φ_1 and φ_2 are staggered against φ_{1a} and φ_{2a} and is consistent with the integration result accounting for eight protons. Model building suggests that the P(1)–Pt–P(1a) angle is at least 120° in order that the large steric and/or electronic strain between these phenyl rings is partially relieved.

Isomerisation is accompanied by slow decomposition to give trace quantities of $[PtCl_2(dppf)]$[5c] [$\delta(^{31}P)$ 13.5, J(Pt–P) 3749 Hz] and $[Cr_2(CO)_{10}(dppf)]$[4] [$\delta(^{31}P)$ 47.3]. Such instability of the heterometallic complex is accentuated in the photolytic degradation of the *trans*-Pt–M complex which afforded mainly $[PtCl_2(dppf)]$, the corresponding chelates and the carbonyl dimers, as expressed by equation (1). Though most *cis*-

$$3[PtCl_2\{M(CO)_5(dppf)\}_2] \xrightarrow{h\nu} 3[PtCl_2(dppf)] + 2[M(CO)_4(dppf)] + [M_2(CO)_{10}(dppf)] + 2[M(CO)_6] \quad (1)$$

$[MCl_2(PR_3)_2]$ (M = Pd or Pt) are well known for their kinetic stability, the neighbouring effect of two sterically demanding groups $(dppf)M(CO)_5$ is probably responsible for the degradation of these heterometallics. For *trans*-$[PdCl_2\{(dppf)Cr(CO)_5\}_2]$ little isomerisation and subsequent decomposition were detected after 1 week of stirring in $CHCl_3$ at room temperature.

---

* At 283 K the peak at $\delta(^1H)$ 4.23 broadens and is subsequently resolved into two sets of multiplets at $\delta(^1H)$ 4.26 and 4.12 at 243 K.

Table 1 Analytical and spectroscopic data for $[M'Cl_x\{(\mu\text{-dppf})M(CO)_5\}_y]$ (M = Cr, Mo or W; M′ = Au, $x = 1, y = 1$; M′ = Pd or Pt, $x = 2, y = 2$)

Complex					Analysis (%)[d]	
M′	M	$\tilde{\nu}$(CO)[a]/cm^{-1}	δ(^{1}H)[b,c]	δ(^{31}P)[b]	C	H
Au	Cr	2064m, 1986w, 1940s	7.47–7.16 (m, 20 H) 4.65 (m, br, 2 H_β^{Au}) 4.36 (m, br, 2 H_β^{Cr}) 4.28 (q, 2 H_α^{Au}) 3.94 (qnt,[e] 2 H_α^{Cr})	47.51 (s, Ph_2PCr) 28.26 (s, Ph_2PAu)	47.85 (47.85)	3.0 (2.9)
Au	Mo	2073m, 1993w, 1947s	7.56–7.26 (m, 20 H) 4.66 (m, br, 2 H_β^{Au}) 4.39 (m, br, 2 H_β^{Mo}) 4.25 (q, 2 H_α^{Au})[f] 3.95 (qnt,[e] 2 H_α^{Mo})	28.53 (s, Ph_2PMo) 28.26 (s, Ph_2PAu)	46.0 (45.8)	2.65 (2.75)
Au	W	2072m, 1986w, 1937s	7.48–7.25 (m, 20 H) 4.68 (m, br, 2 H_β^{Au}) 4.40 (m, br, 2 H_β^{W}) 4.25 (q, 2 H_α^{Au})[f] 3.95 (qnt,[e] 2 H_α^{W})	28.26 (s, Ph_2PAu) 11.30 (t, Ph_2PW) *J*(PW) 244 Hz	42.8 (43.0)	2.5[g] (2.8)
Pd	Cr	2062m, 1986w, 1933s	7.58–7.26 (m, 40 H) 5.07 (m, br, 4 H_β^{Pd}) 4.31 (q, 4 H_α^{Pd})[f] 4.23 (s, br, 8 H^{Cr})	47.51 (s, Ph_2PCr) 14.67 (s, Ph_2PPd)	56.2 (56.1)	3.2 (3.4)
Pd	Mo	2072m, 1991w, 1946s	7.43–7.26 (m, 40 H) 5.06 (m, br, 4 H_β^{Pd}) 4.32 (q, 4 H_α^{Pd}) 4.24 (s, br, 8 H^{Mo})	28.53 (s, Ph_2PMo) 14.67 (s, Ph_2PPd)	53.2 (53.3)	3.1 (3.2)
Pd	W	2071m, 1982w, 1938s	7.53–7.26 (m, 40 H) 5.08 (m, br, 4 H_β^{Pd}) 4.31 (q, 4 H_α^{Pd}) 4.25 (s, br, 8 H^{W})	14.67 (s, Ph_2PPd) 11.24 (t, Ph_2PW) *J*(PW) 247 Hz	48.2 (48.4)	2.7 (2.9)
Pt	Cr	2063m, 1984w, 1940s	7.53–7.28 (m, 20 H)[h] 7.37 (s, br, 20 H) 5.07 (m, br, 4 H_β^{Pt}) 4.33 (m,[i] 4 H_α^{Pt})[f] 4.23 (s, br, 8 H_α^{Cr})[j]	47.3 (s, Ph_2PCr) 10.0 (t, Ph_2PPt) *J*(PPt) 2630 Hz	53.0 (53.3)	3.25 (3.20)
Pt	Mo	2072m, 1990w, 1946s	7.53–7.26 (m, 40 H) 5.05 (m, br, 4 H_β^{Pt}) 4.32 (q, 4 H_α^{Pt})[f] 4.25 (s, br, 8 H^{Mo})	28.40 (s, Ph_2PMo) 10.23 (t, Ph_2PPt) *J*(PPt) 2632 Hz	50.8 (50.7)	2.9 (3.1)
Pt	W	2071m, 1983w, 1937s	7.54–7.33 (m, 40 H) 5.10 (m, br, 4 H_β^{Pt}) 4.33 (q, 4 H_α^{Pt}) 4.26 (s, br, 8 H^{W})	11.04 (t, Ph_2PW) *J*(PW) 244 Hz 10.09 (t, Ph_2PPt) *J*(PPt) 2632 Hz	46.1 (46.3)	2.7 (2.8)

[a] In $CHCl_3$. [b] In $CDCl_3$. Except for M′ = Pt, M = Cr, all the spectra reported were obtained on a 90 MHz machine. [c] H_α and H_β refer to the external and internal cyclopentadienyl protons, H^M denotes the protons of the M-co-ordinated phosphinocyclopentadienyl rings. Spectral assignment is assisted by ^1H–^1H decoupling experiments where necessary. [d] Calculated values are given in parentheses. [e] qnt = quintet. [f] *J*(PH) = 1.71 Hz. [g] Calculated for $[AuCl\{(dppf)W(CO)_5\}]\cdot 0.25C_6H_{14}$. Presence of hexane as the solvent of crystallisation was confirmed by NMR analysis. [h] Recorded on a Bruker WM-250 instrument. The broad singlet at δ 7.37 is assigned to protons on $\varphi_{3,3a}$ while the other signals (δ 7.28–7.53) belong to protons on $\varphi_{1,1a}$ and $\varphi_{2,2a}$; H^{Pt} and H^{Cr} refer to protons on $Cp_{1,1a}$ and $Cp_{2,2a}$ in the text respectively. [i] On a 90 MHz machine this signal was observed as a quartet. [j] This peak broadens at 283 K and is subsequently resolved into two sets of multiplets at δ(^{1}H) 4.26 and 4.12 at 243 K.

An interesting feature in the present synthesis is the formation of a *trans* complex from a *cis* precursor, $[PtCl_2(dmso)_2]$, and the subsequent spontaneous isomerisation to the *cis* complex. A wealth of information is available in the *cis* ⟷ trans isomerisation of complexes of Pd^{II} and Pt^{II}.[8] Formation of the *trans* isomer is understood from the steric and mechanistic viewpoint. Either free phosphine, or adventitious dmso, is responsible for a concerted displacement mechanism for the initial isomerisation to give the *trans* complex.[9] The eventual conversion into the *cis* isomer in the absence of a base (anionic or neutral) and in a solvent of poor donicity like $CDCl_3$ is likely to occur *via* an autocatalytic pathway initiated by the dissociation of the bulky phosphine.[10]

Crystal and Molecular Structure.—In view of the ready isomerisation observed in solution it is necessary for the solid-state structure to be examined in detail. The complex $[PtCl_2\{(dppf)W(CO)_5\}_2]$ was chosen as a representative example because of its highest steric demand and good crystallinity. Single crystals were grown in CH_2Cl_2–hexane as golden-red needles. The structure, which has a crystallographically imposed $\bar{1}$ symmetry, reveals a *trans*-$PtCl_2$ unit sandwiched by two bimetalloligand units $W(CO)_5(dppf)$ (Fig. 1, Tables 2–4). The resultant complex aggregate thus demonstrates a 'linear' array of five metal centres linked exclusively by the phosphinocyclopentadienyl moieties, $C_5H_4PPh_2$. The *trans* configuration is consistent with the solution structure before isomerisation. Contrary to the other platinum(II) complexes,[11] *e.g.* $[PtCl_2(dppf)]$[5c] and $[Pt(S_2N_2)(dppf)]$,[11a] where distortions of the geometry imposed by dppf in a chelational mode were observed, the present complex exhibits near-idealised square-planar geometry for platinum [Cl–Pt–P 87.5(2)–92.5(2), P–Pt–P 180.0(1)°]. The *trans* arrangement of the two $W(CO)_5(dppf)$ ligands helps to ease the inter-ligand repulsion otherwise imposed. Since the observed Pt–P distances [2.325(5) Å] are not indicative of any significant bond weakening as observed in some bulky phosphines,[12] the steric demand of the local $Ph_2PC_5H_4$ site cannot be considered as unfavourably high and

Table 2 Crystallographic data and refinement details for *trans*-$[PtCl_2\{(\mu\text{-dppf})W(CO)_5\}_2]$ and $[Mo(CO)_5(dppf\text{-}P)]$ *

Molecular formula	$PtCl_2[(\mu\text{-dppf})W(CO)_5]_2$	$Mo(CO)_5(dppf\text{-}P)$
M	2022.61	790.40
Colour and habit	Golden-red needles	Gold prism
a/Å	10.73(1)	11.917(3)
b/Å	26.63(3)	11.090(2)
c/Å	13.43(1)	27.10(1)
β/°	106.38(8)	95.92(3)
U	3682.18(6.51)	3562(2)
Z	2	4
$F(000)$	1952	1600
D_c/g cm^{-3}	1.820	1.474
Standard reflections	(2,0,2), (1, −1, −1)	(2,2,2), (3,0,4)
Intensity variation (%)	±1.1	±3
R_{int} (from merging of equivalent reflections)	0.023	0.021
μ/cm^{-1}	56.93	8.79
Crystal size/mm	0.036 × 0.042 × 0.60	0.12 × 0.32 × 0.36
Mean μr	0.113	0.117
Transmission factors	0.733–0.930	0.674–0.790
Scan rate/° min^{-1}	3.02–15.60	2.49–15.63
Scan range	0.70° below Kα1 to 0.80° above Kα2	0.60° below Kα1 to 0.70° above Kα2
$2\theta_{max}$/°	42	55
Unique data measured	4611	8145
Obs. data with $\|F_o > 6\sigma(\|F_o\|)$, n	2728	3919
No. of variables, p	448	433
R_F	0.041	0.036
R_G	0.040	0.044
S	1.252	0.990
Residual extrema in final difference map/e Å^{-3}	+1.14 to −0.70	+0.46 to −0.25

* Details in common: space group $P2_1/c$ (no. 14); ω scans; stationary counts for one-fifth of scan time at each end of scan range, $h,k,\pm l$.

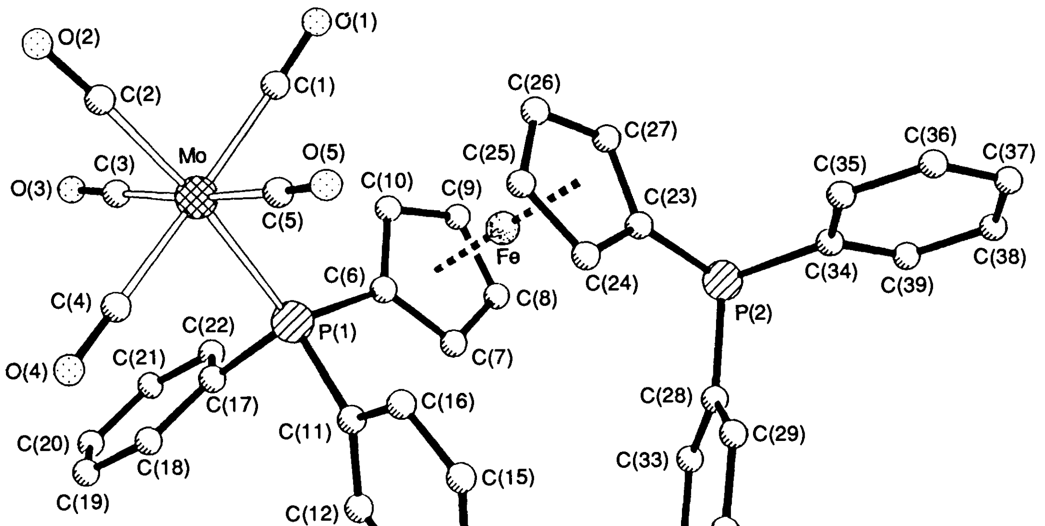

Fig. 2 Molecular structure of $[Mo(CO)_5(dppf\text{-}P)]$

hence the *trans* orientation originates from the spatial diffuseness of the metalloligand as a whole. Similar structure and geometry would be expected for the other Group 6 analogues.

The two phosphinocyclopentadienyl rings are almost parallel (dihedral angle = 5.1°), planar and orientated 9.9° from the idealised eclipsed conformation. The similarity of the twist angle (τ = 153.9°) to that of the molybdenum analogue of its building block *viz.* $[Mo(CO)_5(dppf)]$ (discussed below), despite their vast difference in size, further suggests that the twist angles of the ferrocenyl C_5H_5 rings are dependent as much on crystal packing as on intramolecular forces. This implies that a symmetrical dppf-bridged structure does not necessarily impose an idealised *trans* staggered form. Typical examples can be found in two open-bridged complexes $[M_2(CO)_{10}(\mu\text{-dppf})]$ (M = Cr, τ = 171.6°; M = Mo, τ = 173.2°)[13] and $[\{Re_2(CO)_9\}_2(\mu\text{-dppf})]$ (τ = 131.8°).[2b]

An X-ray diffraction study on the metalloligand $[Mo(CO)_5(dppf\text{-}P)]$ (Fig. 2) allows an examination of the ring conformation of the complex for comparison with that of the free ligand, dppf,[14] and its bidentate form described above. As in the above complex, the two cyclopentadienyl rings are almost parallel (dihedral angle = 2.3°) and planar. A twist angle of 132.5° is well short of the idealised 180° found in free dppf and is the smallest ever found for mono-co-ordinated dppf. This is perhaps unexpected in view of the free rotation which is inherent

Table 3 Selected bond lengths (Å), angles (°) and torsional angles (°)

(*a*) $[PtCl_2\{(\mu\text{-dppf})W(CO)_5\}_2]$

Pt–Cl(1)	2.304(5)
Pt–Cl(1a)	2.304(5)
Pt–P(1)	2.325(5)
Pt–P(1a)	2.325(5)
P(1)–C(13)	1.82(1)
P(2)–C(18)	1.81(1)
W(1)–P(2)	2.546(6)
W(1)–C(41–45)	2.03(2)(mean)
Fe(1)–C(13–17)	2.04(2)(mean)
Fe(1)–C(18–22)	2.04(2)(mean)
C–O	1.15(2)(mean)
Cl(1)–Pt–P(1)	92.5(2)
Cl(1)–Pt–P(1a)	87.5(2)
Cl(1a)–Pt–P(1)	87.5(2)
Cl(1a)–Pt–P(1a)	92.5(2)
P(1)–Pt–P(1a)	180.0(1)
Cl(1)–Pt–Cl(1a)	180.0(1)
Pt–P(1)–C(13)	116.7(5)
W(1)–P(2)–C(18)	115.2(5)
P(2)–W(1)–C(41)	94.1(5)
P(2)–W(1)–C(42)	170.9(4)
P(2)–W(1)–C(43)	90.8(5)
P(2)–W(1)–C(44)	86.9(5)
P(2)–W(1)–C(45)	96.6(5)
Cp1–Fe–Cp2	175.7
C(13)–Cp1–Cp2–C(18)	153.9

Symmetry transformation: a $-x, -y, -z$. Cp1 and Cp2 are the centroids of the rings composed of carbon atoms C(13)–C(17) and C(18)–C(22), respectively

(*b*) $[Mo(CO)_5(\text{dppf-}P)]$

Mo–P(1)	2.563(2)
Mo–C(2)	1.988(6)
Mo–C(1,3,5)	2.038(6)(mean)
P(1)–C(6)	1.813(5)
P(2)–C(23)	1.816(5)
Fe–C(6–10)	2.039(5)(mean)
Fe–C(23–27)	2.036(5)(mean)
Fe–Cp1	1.644(5)
Fe–Cp2	1.642(5)
C(2)–O(2)	1.142(7)
C–O(1,3–5)	1.136(8)(mean)
Mo–P(1)–C(6)	121.8(1)
P(1)–Mo–C(2)	171.4(2)
C(2)–Mo–C(1,3–5)	88.1(2)(mean)
Cp1–Fe(1)–Cp2	177.4(2)
C(6)–Cp1–Cp2–C(23)	132.5

Cp1 is the centre of the ring composed of carbon atoms C(6)–C(10), Cp2 the centre of C(23)–C(27), respectively.

in a pendant-phosphine site. However, as shown by the data associated with the ferrocenyl moiety, no unusual strain in the molecule is apparent and the non-linear twist is probably decided by lattice forces. There is however no evidence to suggest the retention of such ring orientation in solution. The near-constant ^{31}P shifts which we found for all pendant-phosphine complexes and the insensitivity of the co-ordination shift to criteria other than the nature of the co-ordinated metal are suggestive of possibly a staggered *trans* disposition of the two phosphorus sites in bridging and unidentate dppf complexes in solution. Consequently, the staggered–eclipsed relationship is lattice-dependent, except in chelating dppf where the eclipsed and staggered configurations are favoured in the tetrahedral and planar (or octahedral) metal geometries respectively.[5,11,14]

Electrochemistry.—In general, for the oxidation of the present complexes, two waves are observed with a third very close to the solvent-breakdown limit. The latter wave (1.275–1.400 V) shows poor reproducibility and the peak is not well defined. The results are summarised in Table 5.

The first wave is close to reversibility for the Au–M complexes and chemically stable and quasi-reversible for the heteropolymetallics of Pt and Pd. The first oxidation peak is ferrocene-based as evidenced from the electrochemistry of dppf-substituted complexes.[15] For Pd/Pt–M complexes, linear-sweep voltammetry and chronoamperometry[16] revealed a one-electron transfer.* While this is anticipated for the Au–M series, it is unexpected for the palladium or platinum analogues where there are two *trans*-oriented ferrocenyl entities. We attribute this to the bulky and linear-propagated nature of the pentametallics which preclude a simultaneous approach of both ferrocenyl sites to the electrode. The second wave resembles that for $[M(CO)_5\{PPh_2(C_5H_4FeC_5H_5)\}]$ reported by Kotz *et al.*[17a] and is attributable to the oxidation of the carbonyl metal centres which could be accompanied by electron loss from the M–P bonds.[17] In all cases, no corresponding reduction peak is observed upon scan reversal, thus suggesting an unstable product. The height of the wave is approximately double that of the first wave which implies a two-electron step. The third peak signifies complex degradation, possibly due to oxidation of M (Au^I and Pt^{II} or Pd^{II}) accompanied by phosphorus cleavage.[18]

The similar potentials registered for all the complexes are consistent with the isostructural and isoelectronic relationship for complexes of the same congener group (Cr, Mo and W or Pd and Pt) and that the redox behaviour of the first wave registered is ferrocene-based. The presence of a strong π-acid ligand such as CO is also expected to induce a mediating effect on the changes exerted by the metal effects. Nevertheless, the formal potentials registered for the gold(I) complexes are generally higher than those of the complexes of Pd^{II} and Pt^{II}. The *trans* disposition of the phosphine ligands in the latter square-planar complexes weakens the M–P linkages and reduces the electron donation from dppf. This accounts for the cathodic shift for the complexes of Pd^{II} and Pt^{II} and renders them more susceptible to oxidation with respect to the gold(I) complexes. The complexes of Pd^{II} generally display a higher formal potential than those of Pt^{II}, which is in line with the expected higher resistivity to oxidation for a lighter congener of a group.[19] For the same reason, the formal potentials of the chromium complexes are higher than those of Mo. The tungsten heterometallics with Pd^{II} or Pt^{II} however display unusually high anodic shifts. We attribute this anomaly to the steric hindrance attenuated by the bulky $W(CO)_5$ moieties which disturbs the approach of the substrate to the electrodes.

Experimental

General.—All procedures were performed under pure dry nitrogen or argon using standard Schlenk techniques. The general procedures and instruments used followed those described in our earlier reports.[2a–c,4] The complexes $[AuCl(SMe_2)]$,[20] *trans*-$[PdCl_2(PhCN)_2]$[21] and *cis*-$[PtCl_2(dmso)_2]$[22] were synthesised as previously described.

Syntheses.—$[M(CO)_5(\text{dppf-}P)]$ (M = Cr, Mo *or* W). Syntheses of these complexes have been reported previously.[4] A higher yield of the complexes of Cr and Mo was obtained as follows. The complex $[M(CO)_6]$ (M = Cr or Mo) (0.5 g) was stirred in MeCN (20 cm^3) *in vacuo* with $Me_3NO{\cdot}2H_2O$ in a

---

* Chronoamperometric and linear-sweep voltammetric experiments were carried out on two representative complexes, Pd–Cr and Pt–W [the smallest and largest in size for the palladium(II), platinum(II) series]. The method employed here assumes reversibility of the electrochemical reaction. At low scan rate (10 mV s^{-1}) both systems are quite close to reversibility (ΔE_p 100 mV for Pd–Cr, 96 mV Pt–W, 70 mV for ferrocene in both cases), *n* (number of electron transfers) was determined to be one for both the Pd–Cr and Pt–W complexes.

Table 4 Atomic coordinates (× 10^5 for Pt, W, Mo and Fe, × 10^4 for other atoms)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*a*) $[PtCl_2\{(\mu\text{-dppf})W(CO)_5\}_2]$							
Pt	50 000	0	50 000	C(20)	1 988(14)	655(5)	3 044(11)
W(1)	−58(7)	22 845(3)	7 604(5)	C(21)	2 111(14)	275(6)	2 342(10)
Fe(1)	3 148(2)	891(1)	2 161(2)	C(22)	1 610(13)	476(5)	1 342(11)
Cl(1)	3 981(4)	393(2)	6 084(3)	C(23)	−1 158(16)	1 059(6)	−164(11)
P(1)	5 680(4)	759(2)	4 473(3)	C(24)	−1 653(15)	775(7)	503(13)
P(2)	386(4)	1 382(2)	303(3)	C(25)	−2 903(18)	573(7)	188(15)
C(1)	7 411(13)	751(6)	4 650(10)	C(26)	−3 704(20)	647(8)	−824(17)
C(2)	8 201(15)	478(6)	5 454(11)	C(27)	−3 207(17)	916(8)	−1 500(15)
C(3)	9 528(17)	490(6)	5 638(13)	C(28)	−1 967(15)	1 119(6)	−1 173(11)
C(4)	10 119(19)	772(7)	5 042(16)	C(29)	1 225(14)	1 236(7)	−671(11)
C(5)	9 334(17)	1 038(8)	4 236(16)	C(30)	1 085(17)	783(7)	−1 181(3)
C(6)	7 993(15)	1 026(7)	4 024(13)	C(31)	1 843(21)	667(10)	−1 841(15)
C(7)	5 448(16)	1 317(6)	5 176(10)	C(32)	2 753(23)	1 008(10)	−1 963(17)
C(8)	6 482(17)	1 560(6)	5 853(13)	C(33)	2 897(18)	1 460(9)	−1 477(14)
C(9)	6 319(18)	1 961(7)	6 438(14)	C(34)	2 165(16)	1 571(7)	−800(12)
C(10)	5 099(20)	2 136(7)	6 344(15)	C(41)	−1 784(9)	2 328(7)	−294(11)
C(11)	4 017(19)	1 902(8)	5 716(16)	C(42)	−261(17)	2 964(3)	1 360(12)
C(12)	4 224(19)	1 509(7)	5 124(14)	C(43)	1 765(8)	2 308(7)	1 826(9)
C(13)	5 012(13)	925(6)	3 108(10)	C(44)	−951(14)	1 995(7)	1 750(10)
C(14)	4 924(15)	598(6)	2 267(10)	C(45)	703(15)	2 616(6)	−332(9)
C(15)	4 489(14)	884(7)	1 347(12)	O(41)	−2 765(11)	2 370(6)	−909(10)
C(16)	4 284(16)	1 389(7)	1 612(12)	O(42)	−331(13)	3 336(4)	1 742(9)
C(17)	4 562(14)	1 405(6)	2 690(11)	O(43)	2 757(10)	2 366(5)	2 445(8)
C(18)	1 203(14)	989(6)	1 391(10)	O(44)	−1 574(11)	1 846(5)	2 247(9)
C(19)	1 472(13)	1 097(6)	2 480(10)	O(45)	1 008(13)	2 830(5)	−974(9)
(*b*) $[Mo(CO)_5(dppf\text{-}P)]$							
Mo	42 309(4)	22 806(4)	7 898(2)	C(16)	6 249(4)	3 764(5)	1 917(2)
Fe	81 478(5)	35 587(5)	7 336(2)	C(17)	6 216(4)	202(4)	1 413(2)
P(1)	6 156(1)	1 825(1)	1 265(1)	C(18)	5 604(5)	−264(5)	1 771(2)
P(2)	10 476(1)	5 292(1)	1 043(1)	C(19)	5 555(6)	−1 502(6)	1 838(3)
O(1)	5 126(3)	3 285(4)	−200(2)	C(20)	6 116(6)	−2 257(6)	1 564(3)
O(2)	1 798(4)	2 356(4)	233(2)	C(21)	6 712(6)	−1 820(5)	1 210(3)
O(3)	4 261(4)	−415(4)	395(2)	C(22)	6 779(5)	−581(4)	1 136(2)
O(4)	3 079(4)	1 605(4)	1 751(2)	C(23)	8 983(4)	5 158(4)	835(2)
O(5)	3 926(4)	5 001(4)	1 102(2)	C(24)	8 019(4)	5 132(4)	1 102(2)
C(1)	4 854(4)	2 902(5)	158(2)	C(25)	7 052(4)	4 973(4)	760(2)
C(2)	2 690(5)	2 372(5)	433(2)	C(26)	7 404(4)	4 870(4)	282(2)
C(3)	4 281(4)	539(5)	540(2)	C(27)	8 587(4)	4 979(4)	323(2)
C(4)	3 514(5)	1 812(5)	1 409(2)	C(28)	10 491(4)	5 090(5)	1 719(2)
C(5)	4 069(4)	4 012(6)	1 002(2)	C(29)	9 950(5)	5 828(6)	2 023(2)
C(6)	7 460(3)	2 026(4)	985(2)	C(30)	9 983(7)	5 604(8)	2 527(3)
C(7)	8 557(4)	2 230(4)	1 236(2)	C(31)	10 582(8)	4 635(10)	2 723(3)
C(8)	9 341(4)	2 249(4)	882(2)	C(32)	11 137(8)	3 910(8)	2 434(3)
C(9)	8 758(4)	2 056(4)	413(2)	C(33)	11 097(6)	4 121(6)	1 929(3)
C(10)	7 596(4)	1 925(4)	465(2)	C(34)	10 689(4)	6 924(4)	992(2)
C(11)	6 519(4)	2 572(4)	1 862(2)	C(35)	9 836(5)	7 764(5)	900(2)
C(12)	7 154(5)	2 027(6)	2 252(2)	C(36)	10 090(6)	8 970(5)	849(2)
C(13)	7 524(6)	2 657(7)	2 670(2)	C(37)	11 171(6)	9 340(6)	880(2)
C(14)	7 272(5)	3 851(7)	2 712(2)	C(38)	12 037(6)	8 530(6)	969(2)
C(15)	6 629(5)	4 417(5)	2 335(2)	C(39)	11 792(4)	7 324(5)	1 016(2)

ratio of 1:0.8 for 45–60 min, during the course of which the infrared spectrum was taken to check for the disappearance of $[M(CO)_6]$. The mixture was then added dropwise to a tetrahydrofuran (thf) solution (25 cm^3) of dppf (Cr:dppf = 1:1; Mo:dppf = 1.0:1.2) and was stirred for another 15 min before the solvent was removed *in vacuo*. Separation was achieved by preparative TLC as described in earlier reports.[2a–c,4] Yields: 39 (M = Cr), 31% (Mo) (based on dppf consumed).

$[AuCl\{(\mu\text{-dppf})M(CO)_5\}]$. The complex $[M(CO)_5(dppf)]$ (0.05 g) in thf (10 cm^3) was added dropwise *via* a polytetrafluoroethylene filtering device to solid $[AuCl(SMe_2)]$ (1:1 ratio). The mixture was stirred for 3 h, after which sufficient absolute alcohol was added to precipitate the orange-yellow product. The filtered crude product was dissolved in the minimum of thf and was loaded on a silica gel column (230–400 mesh ASTM), and separated by flash column chromatography under an argon pressure of about 0.05 MPa with a eluent of chloroform–hexane (30:70). The eluate was concentrated and cooled to 5 °C to induce crystallisation. Yields: 48 (M = Cr), 41 (Mo) and 64% (W).

trans-$[PdCl_2\{(\mu\text{-dppf})M(CO)_5\}_2]$. The complex $[M(CO)_5(dppf)]$ (0.05 g) was dissolved in the minimum quantity of thf and transferred dropwise through a filtering tube to a thf solution (5 cm^3) of *trans*-$[PdCl_2(PhCN)_2]$ in a reactant ratio of 2:1. More thf was added to give a total volume of 15 cm^3 and the orange reaction mixture was stirred for 15 min. The solution was then filtered, concentrated *in vacuo*, and sufficient absolute alcohol was added to facilitate product precipitation. The mixture was kept at *ca.* −20 °C for several hours, after which the bright orange deposits (43–45% yield for all the three complexes) were filtered off.

When a solution of *trans*-$[PdCl_2\{(\mu\text{-dppf})Cr(CO)_5\}_2]$ in $CHCl_3$ [$\delta(^{31}P)$ 14.2, 47.1] was stirred for 1 week at room temperature the ^{31}P NMR spectrum ($CDCl_3$, 300 MHz)

Table 5 Cyclic voltammetric data for the first two waves of the complexes [$M'Cl_x\{(\mu\text{-dppf})M(CO)_5\}_y$] ($M$ = Cr, Mo, W; M' = Au, $x = y = 1$; M' = Pd or Pt, $x = y = 2$)

Complex					
M′	M	E_{pa}/V	$E_{pc}{}^a$/V	$E^{\circ\prime a}$/V	$\Delta E_p{}^a$/mV
Au	Cr	0.810^a 1.140^b	0.729	0.7695	81
Au	Mo	0.809^a 1.130^b	0.721	0.765	88
Au	W	0.797^a 1.140^b	0.716	0.7565	81
Pd	Cr	0.709^a 1.138^b	0.598	—	111
Pd	Mo	0.705^a 1.115^b	0.597	—	108
Pd	W	0.728^a 1.150^b	0.625	—	113
Pt	Cr	0.692^a 1.099^b	0.599	—	93
Pt	Mo	0.691^a 1.130^b	0.592	—	99
Pt	W	0.710^a 1.180^b	0.600	—	110
	dppf	0.400^c	0.315	0.3575	85

^{a} Scan rate 50 mV s^{-1}. ^{b} Scan rate 100 mV s^{-1}. Peak is irreversible. ^{c} Scan rate 100 mV s^{-1}.

revealed the formation of trace amounts of [$PdCl_2$(dppf)] [$\delta(^{31}P)$ 34.1] and [$Cr_2(CO)_{10}$(dppf)] [$\delta(^{31}P)$ 47.1].

trans-[$PtCl_2\{(\mu\text{-dppf})M(CO)_5\}_2$]. The complex [$M(CO)_5$(dppf)] (0.05 g) was dissolved in thf (40 cm^3) to give an orange-yellow solution to which solid *cis*-[$PtCl_2(dmso)_2$] (M : Pt = 1 : 0.5) was introduced. The mixture was stirred for 2–3 h after which the volume was reduced by half in vacuum. Sufficient absolute alcohol was introduced to precipitate the orange-yellow product. The crude products for M = Mo or W were further purified by flash chromatography as described earlier using 30% chloroform in hexane as eluent. The collected eluate was then left to crystallise at 5 °C. Yields of 45, 33 and 29% were obtained for the complexes of Cr, Mo and W respectively.

When $K_2[PtCl_4]$ dissolved in the minimum of deionised water was added to [$M(CO)_5$(dppf)] (M = Mo or W) in absolute alcohol (50 cm^3) at 60 °C the reaction mixture immediately became turbid. The reaction mixture was stirred for 3 h at room temperature (M = Mo) or overnight (M = W), after which the precipitate formed was filtered off and recrystallised from CH_2Cl_2–hexane. NMR (^1H and ^{31}P) spectroscopy showed that the same *trans* complexes were formed.

When a solution of *trans*-[$PtCl_2\{(\mu\text{-dppf})Cr(CO)_5\}_2$] in $CDCl_3$ [$\delta(^{31}P)$ 10.0, J(Pt–P) 2630 Hz; $\delta(^{31}P)$ 47.3] was allowed to stand for 21 h at room temperature the ^{31}P NMR spectrum revealed the formation of *cis*-[$PtCl_2\{(\mu\text{-dppf})Cr(CO)_5\}_2$] [$\delta(^{31}P)$ 9.5, J(Pt–P) 3976 Hz; $\delta(^{31}P)$ 47.0], $PtCl_2$(dppf) [$\delta(^{31}P)$ 13.5, J(Pt–P) 3749 Hz], and [$Cr_2(CO)_{10}(\mu\text{-dppf})$] [$\delta(^{31}P)$ 47.3].

NMR Studies on trans-[$PtCl_2\{(\mu\text{-dppf})Cr(CO)_5\}_2$].—All NMR spectra were recorded on a Bruker WM-250 superconducting Fourier-transform spectrometer operating at 250.133 MHz for ^1H and 101.256 MHz for ^{31}P nuclei using 5 mm (outside diameter) tube in $CDCl_3$ and with $SiMe_4$ as internal standard. The standard 90° pulses were 8.5 and 20.0 s for the two different nuclei. Data processing for two-dimensional experiments was carried out on a Bruker ASPECT-3000 data system. A sine bell window function was selected with a zero-degree shift for both dimensions and with zero-filling (512 W) in the second dimension. A mixing time of 0.1 s was used for two dimensional nuclear Overhauser effect spectroscopy (NOESY). Accurate chemical shifts for $Cp_{1,1a}$ were derived from the two-dimensional J-resolved spectrum.

UV-Photolytic Experiments.—All the experiments were carried out under an argon atmosphere. The complex *trans*-[$M'Cl_2\{(\mu\text{-dppf})M(CO)_5\}_2$] (M = Cr, Mo or W; M′ = Pd or Pt) (10–30 mg) was dissolved in thf–hexane (1.0 : 7.5, 20–30 cm^3) in a round-bottomed Pyrex flask (100 cm^3) and was photolysed at 0 °C for 30–60 min using a vapour-arc high-pressure mercury lamp (225.1–313.1 nm, arc size 19 × 6 mm) externally placed at *ca.* 5 cm from the reaction flask. The reaction mixture was monitored periodically by TLC. The products formed were identified *in situ* spectroscopically (^1H and ^{31}P NMR). In some of the experiments, *e.g.* when M = Cr and M′ = Pd or Pt, reddish brown and yellow precipitates were respectively formed during the course of photolysis. These deposits were filtered off, washed with hexane, and identified as the corresponding [$M'Cl_2$(dppf)] by NMR spectroscopy. The amount of chelate [$M(CO)_4$(dppf)] produced is dependent on the ease of chelation of the metals.[23] A commonly formed by-product of the photolysis is [$M(CO)_5\{Ph_2P(C_5H_4)Fe(C_5H_4)PPh_2O\}$].[24]

X-Ray Crystallographic Analysis.—Single crystals of both [$PtCl_2\{(\mu\text{-dppf})W(CO)_5\}_2$] and [$Mo(CO)_5$(dppf-$P$)] were grown from CH_2Cl_2–hexane, the former at 25 and the latter at 5 °C. Those suitable for X-ray diffraction were mounted on thin-walled Lindemann glass capillaries under an atmosphere of nitrogen. Measurements were made on a Nicolet R3m/v diffractometer using graphite-monochromatised Mo-Kα radiation (λ 0.710 73 Å). The determination of the crystal class, orientation matrix and cell dimensions was performed according to established procedures.[25] Crystal data, data collection parameters and the results of the analysis are listed in Table 2. Crystals of the platinum complex are long, fine needles which are easily shattered by cutting. A usable specimen was chosen after examination of a number of single crystals. This resulted in the poor estimated standard deviation (e.s.d.s) in the unit-cell dimension. All data processing was performed on a DEC MicroVax-II computer with the SHELXTL-PLUS program package.[26] Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[27] The raw data were processed with the learnt-profile procedure[28] and absorption corrections were applied by fitting a pseudo-ellipsoid to the ω-scan data of selected reflections over a range of two θ angles.[29]

Both structures were solved with the Patterson superposition method. The positions of all hydrogen atoms were generated geometrically (C–H bonds fixed at 0.096 Å), assigned isotropic thermal parameters and allowed to ride on their respective parent C atoms.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Electrochemical Measurements.—Cyclic voltammetric measurements were made with a PARC (EG & G) model 264A voltammetric analyser and were recorded on a model WX2300 (Graphtec Corp., Tokyo, Japan) x–y recorder. All experiments were performed in AnalaR grade CH_2Cl_2 which was distilled over P_2O_5 before use with 0.15 mol dm^{-3} tetrabutylammonium perchlorate as supporting electrolyte. The reference electrode was Ag–Ag$^+$ (0.01 mol dm^{-3} Ag$^+$, 0.1 mol dm^{-3} NBu_4BF_4 in acetonitrile). The working electrode was either a planar platinum-disc electrode (1 mm diameter) or a glassy carbon disc electrode (diameter 3 mm); the counter electrode was a coiled platinum wire. All experiments were carried out at ambient temperature (25 ± 2 °C).

Acknowledgements

The authors acknowledge the National University of Singapore (NUS) (RP850030) and Hong Kong UPGC Earmarked Grant

(Research Acc. No. 221600010) for financial support and technical assistance from the Department of Chemistry, NUS. L.-T. P. thanks NUS for a scholarship award.

References

1 Part 20, T. S. A. Hor, P. M. N. Low, Y. K. Yan, L.-K. Liu and Y.-S. Wen, *J. Organomet. Chem.*, in the press.

2 (*a*) Y. K. Yan, H. S. O. Chan, T. S. A. Hor, K.-L. Tan, L.-K. Liu and Y.-S. Wen, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 423; (*b*) T. S. A. Hor, H. S. O. Chan, K.-L. Tan, L.-T. Phang, Y. K. Yan, L.-K. Liu and Y.-S. Wen, *Polyhedron*, 1991, **10**, 2437; (*c*) H. S. O. Chan, T. S. A. Hor, L.-T. Phang and K.-L. Tan, *J. Organomet. Chem.*, 1991, **407**, 353; (*d*) K. B. H. Lim, L.-T. Phang, M. R. Khan, T. S. A. Hor and H. K. Lee, *J. Chromatogr.*, 1991, **538**, 492; (*e*) T. S. A. Hor and L.-T. Phang, *Bull. Sing. Nat. Inst. Chem.*, 1990, **18**, 29 and refs. therein; (*f*) A. Houlton, S. K. Ibrahim, J. R. Dilworth and J. Silver, *J. Chem. Soc.*, *Dalton Trans.*, 1990, 2421 and refs. therein; (*g*) M. I. Bruce, W. R. Cullen, P. A. Humphrey, O. bin Shawkataly, M. R. Snow and E. R. T. Tiekink, *Organometallics*, 1990, **9**, 2910; (*h*) U. Casellato, B. Corain, R. Graziani, B. Longato and G. Pilloni, *Inorg. Chem.*, 1990, **29**, 1193 and refs. therein: (*i*) G. Pilloni, R. Graziani, B. Longato and B. Corain, *Inorg. Chim. Acta*, 1991, **190**, 165.

3 (*a*) G. B. Jacobsen, B. L. Shaw and M. Thornton-Pett, *J. Chem. Soc.*, *Chem. Commun.*, 1986, 13; *J. Chem. Soc.*, *Dalton Trans.*, 1987, 1509, 2751; (*b*) W. S. McDonald, P. G. Pringle and B. L. Shaw, *J. Chem. Soc.*, *Chem. Commun.*, 1982, 861; (*c*) P. G. Pringle and B. L. Shaw, *J. Chem. Soc.*, *Chem. Commun.*, 1982, 956; (*d*) R. L. Keiter, K. M. Fasig and L. W. Cary, *Inorg. Chem.*, 1975, **14**, 201.

4 T. S. A. Hor and L.-T. Phang, *J. Organomet. Chem.*, 1989, **373**, 319.

5 (*a*) T. Hayashi, M. Konishi, Y. Kobori, M. Kumuda, T. Higuchi and K. Hirotsu, *J. Am. Chem. Soc.*, 1984, **106**, 158; (*b*) I. R. Butler, W. R. Cullen, T.-J. Kim, S. J. Rettig and J. Trotter, *Organometallics*, 1985, **4**, 972; (*c*) D. A. Clemente, G. Pilloni, B. Corain, B. Longato and M. Tiripicchio-Camellini, *Inorg. Chim. Acta*, 1986, **115**, L9; (*d*) C. E. Housecroft, S. M. Owen, P. R. Raithby and B. A. M. Shaykh, *Organometallics*, 1990, **9**, 1617.

6 (*a*) S. O. Grim, R. L. Keiter and W. McFarlane, *Inorg. Chem.*, 1967, **6**, 1133; (*b*) G. K. Anderson and R. J. Cross, *Chem. Soc. Rev.*, 1980, **9**, 185 and refs. therein.

7 P. S. Pregosin, in *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis: Organic Compounds and Metal Complexes*, eds. J. G. Verkade and L. D. Quin, VCH, Deerfield Beach, FL, 1987, ch. 14, pp. 510–515; Z.-Y. Yang, X.-W. Han, T.-X. Li and Y.-R. Song, *Kexue Tongbao*, 1985, **30**, 1490.

8 D. M. Roundhill, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 5, ch. 52, p. 497.

9 W. J. Louw, R. van Eldik and H. Kelm, *Inorg. Chem.*, 1980, **19**, 2878 and refs. therein; A. W. Verstuyft and J. H. Nelson, *Inorg. Chem.*, 1975, **14**, 1501.

10 W. J. Louw and R. van Eldik, *Inorg. Chem.*, 1981, **20**, 1939 and refs. therein.

11 (*a*) P. F. Kelly, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *Polyhedron*, 1988, **7**, 1925; (*b*) B. Longato, G. Pilloni, G. Valle and B. Corain, *Inorg. Chem.*, 1988, **27**, 956; (*c*) A. L. Bandini, G. Banditelli, M. A. Cinellu, G. Sanna, G. Minghetti, F. Demartin and M. Manassero, *Inorg. Chem.*, 1989, **28**, 404.

12 E. C. Alyea, S. A. Dias, G. Ferguson and P. J. Roberts, *J. Chem. Soc.*, *Dalton Trans.*, 1979, 948; N. W. Alcock and P. G. Leviston, *J. Chem. Soc.*, *Dalton Trans.*, 1974, 1834; A. Del Pra and G. Zanotti, *Inorg. Chim. Acta*, 1980, **39**, 137; G. G. Messmer and E. L. Amma, *Inorg. Chem.*, 1966, **5**, 1775; P. B. Hitchcock, B. Jacobson and A. Pidcock, *J. Chem. Soc.*, *Dalton Trans.*, 1977, 2038.

13 T. S. A. Hor, L.-T. Phang, L.-K. Liu and Y.-S. Wen, *J. Organomet. Chem.*, 1990, **397**, 29.

14 U. Casellato, D. Ajo, G. Valle, B. Corain, B. Longato and R. Graziani, *J. Crystallogr. Spectrosc. Res.*, 1988, **18**, 583.

15 D. L. Dubois, C. W. Eigenbrot, jun., A. Miedaner, J. C. Smart and R. C. Haltiwanger, *Organometallics*, 1986, **5**, 1405; B. Corain, B. Longato, G. Favero, D. Ajó, G. Pilloni, U. Russo and F. R. Kreissl, *Inorg. Chim. Acta*, 1989, **157**, 259; T. M. Miller, K. J. Ahmed and M. S. Wrighton, *Inorg. Chem.*, 1989, **28**, 2347; G. Pilloni, B. Longato and B. Corain, *J. Organomet. Chem.*, 1991, **420**, 57; M. Maekawa, S. Kitagawa and M. Munakata, *Kinki Daigaku Rikogakubu Kenkyu Hokoku*, 1989, 103.

16 P. A. Malachesky, *Anal. Chem.*, 1969, **41**, 1493.

17 (*a*) J. C. Kotz, C. L. Nivert, J. M. Lieber and R. C. Reed, *J. Organomet. Chem.*, 1975, **91**, 87; (*b*) J. C. Kotz and C. L. Nivert, *J. Organomet. Chem.*, 1973, **52**, 387; (*c*) G. Distefano, G. Innorta, S. Pignataro and A. Foffani, *J. Organomet. Chem.*, 1968, **14**, 165; (*d*) M. K. Lloyd, J. A. McCleverty, D. G. Orchard, J. A. Connor, M. B. Hall, I. H. Hillier, E. M. Jones and G. K. McEwen, *J. Chem. Soc.*, *Dalton Trans.*, 1973, 1743.

18 J. E. Anderson, S. M. Sawtelle and C. E. McAndrews, *Inorg. Chem.*, 1990, **29**, 2627.

19 C. J. Pickett, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 1, ch. 8.3, pp. 493–501.

20 P. C. Ray and D. C. Sen, *J. Indian Chem. Soc.*, 1930, **7**, 67; K. C. Dash and H. Schmidbaur, *Chem. Ber.*, 1973, **106**, 1221.

21 M. S. Kharasch, R. C. Seyler and F. R. Mayo, *J. Am. Chem. Soc.*, 1938, **60**, 882.

22 J. H. Price, A. N. Williamson, R. F. Schramm and B. B. Wayland, *Inorg. Chem.*, 1972, **11**, 1280.

23 T. S. A. Hor and L.-T. Phang, *Thermochim. Acta*, 1991, **178**, 287; J. A. Connor and G. A. Hudson, *J. Organomet. Chem.*, 1974, **73**, 351.

24 T. S. A. Hor and L.-T. Phang, unpublished work.

25 R. A. Sparks, in *Crystallographic Computing Techniques*, ed. F. R. Ahmed, Munksgaard, Copenhagen, 1976.

26 G. M. Sheldrick, in *Computational Crystallography*, ed. D. Sayre, Oxford University Press, New York, 1982, pp. 506; *Crystallographic Computing 3: Data collection, structure determinationa, proteins and databases*, eds. G. M. Sheldrick, C. Kruger and R. Goddard, Oxford University Press, New York, 1982, pp. 175.

27 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

28 R. Diamond, *Acta Crystallogr.*, *Sect. A*, 1969, **27**, 43.

29 G. Kopfmann and R. Huber, *Acta Crystallogr.*, *Sect. A*, 1968, **24**, 348.

Received 7*th April* 1992; *Paper* 2/01839J