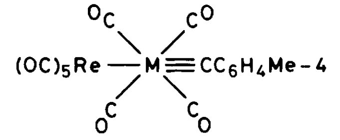
Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 45.[1] Synthesis of the Pentanuclear Metal Complexes $[M'M_2Re_2(\mu-CC_6H_4Me-4)_2(CO)_{18}]$ (M' = Ni or Pt, M = Cr or W) and Related Compounds; *X*-Ray Crystal Structure of $[ReWPt(\mu-CC_6H_4Me-4)(CO)_9(PMe_3)_2]$*

John C. Jeffery, Diane B. Lewis, Gregg E. Lewis, Michael J. Parrott, and F. Gordon A. Stone
Department of Inorganic Chemistry, The University, Bristol BS8 1TS

The pentanuclear metal compounds $[M'M_2Re_2(\mu-CC_6H_4Me-4)_2(CO)_{18}]$ (M' = Pt or Ni, M = Cr or W) have been prepared by treating the complexes $[ReM(\equiv CC_6H_4Me-4)(CO)_9]$ with $[Pt(C_2H_4)_3]$ or $[Ni(cod)_2]$ (cod = cyclo-octa-1,5-diene), respectively. Similarly, the species $[ReM(\equiv CC_6H_4Me-4)(CO)_9]$ react with the platinum compounds $[Pt(C_2H_4)_2\{P(cyclo-C_6H_{11})_3\}]$ and $[Pt(C_2H_4)(PMe_3)_2]$ to afford the trimetal complexes $[ReWPt(\mu-CC_6H_4Me-4)(CO)_{10}\{P(cyclo-C_6H_{11})_3\}]$ and $[ReMPt(\mu-CC_6H_4Me-4)(CO)_9(PMe_3)_2]$ (M = Cr or W), respectively. An *X*-ray diffraction study on the compound $[ReWPt(\mu-CC_6H_4Me-4)(CO)_9(PMe_3)_2]$ shows that the molecule has a bent Re–W–Pt [151.3(1)°] spine, with metal–metal distances Re–W 3.082(1) and W–Pt 2.771(1) Å. The W–Pt bond is bridged by the CC_6H_4Me-4 group [μ-C–W 2.013(24), μ-C–Pt 1.962(23) Å]. The rhenium atom is ligated by five CO groups orthogonally disposed, so that the metal is in an octahedral environment, the sixth site being occupied by the Re–W bond. The platinum atom carries the two PMe_3 ligands [P–Pt–P 98.6(2)°] and the tungsten atom four CO groups. The latter are radially disposed so that the tungsten is in a distorted octahedral environment with respect to these CO ligands, the $Re(CO)_5$ group, and the mid-point of the μ-C–Pt bond [Re–W–μ-C 163.1(6), Re–W–Pt 151.3(1)°]. The radial CO groups on rhenium and tungsten are staggered with respect to each other about the Re–W bond.

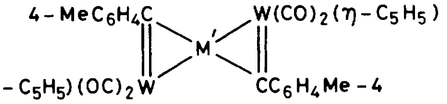
The compounds $[ReM(\equiv CC_6H_4Me-4)(CO)_9]$ (**1**, M = Cr, Mo, or W) are potentially useful precursors for the synthesis of heteronuclear metal cluster complexes. The C≡M groups which are present would be expected to combine with low-valent metal–ligand fragments, as does the C≡W group in $[W(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5H_5)]$.[2] In agreement with this idea, we have recently shown that the compounds (**1**) react with $[Co_2(CO)_8]$ to afford tetranuclear metal clusters $[Co_2MRe(\mu_3-CC_6H_4Me-4)(CO)_{15}]$.[3] On heating in toluene the latter release a carbonyl fragment containing the Group 6 metal and yield $[Co_2Re(\mu_3-CC_6H_4Me-4)(CO)_{10}]$. Herein we describe reactions of the complexes (**1a**) and (**1c**) with some zero-valent platinum and nickel species.



	M
(**1a**)	Cr
(**1b**)	Mo
(**1c**)	W

Results and Discussion

Earlier work[4] has shown that reactions between one equivalent of $[Pt(C_2H_4)_3]$ or $[Ni(cod)_2]$ (cod = cyclo-octa-1,5-diene) and two equivalents of $[W(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5H_5)]$ give the trimetal compounds $[M'W_2(\mu-CC_6H_4Me-4)_2(CO)_4(\eta-C_5H_5)_2]$ (**2**, M = Ni or Pt). In these products nickel or platinum atoms are ligated by two C≡W groups in a manner related to the alkyne–platinum bonding in the compounds $[Pt(RC_2R)_2]$ (R = alkyl or aryl).[5] These results suggested that it might be possible to prepare pentanuclear metal compounds $[M'M_2Re_2(\mu-CC_6H_4Me-4)_2(CO)_{18}]$ (**3**, M' = Pt or Ni, M = Cr or W) structurally related to the trimetal complexes (**2**).



	M'
(**2a**)	Ni
(**2b**)	Pt

Treatment of (**1a**) with $[Pt(C_2H_4)_3]$, generated *in situ* from $[Pt(cod)_2]$, gave the red complex $[Re_2Cr_2Pt(\mu-CC_6H_4Me-4)_2(CO)_{18}]$ (**3a**). A similar reaction between (**1c**) and $[Pt(C_2H_4)_3]$ afforded $[Re_2W_2Pt(\mu-CC_6H_4Me-4)_2(CO)_{18}]$ (**3b**). Both (**3a**) and (**3b**) were characterised by microanalysis (Table 1), and by their ^1H and $^{13}C-\{^1H\}$ n.m.r. spectra (Table 2). In particular, the $^{13}C-\{^1H\}$ n.m.r. spectra showed characteristic[6] resonances for alkylidyne carbon nuclei bridging metal–metal bonds [(**3a**), δ 331.5; (**3b**), 298.2 p.p.m.]. Moreover, in the spectrum of (**3b**) strong $^{195}Pt-^{13}C$ coupling (844 Hz) was observed, as seen in other molecules with $\overline{W(\mu-C)Pt}$ ring systems.[7,8] In each

---

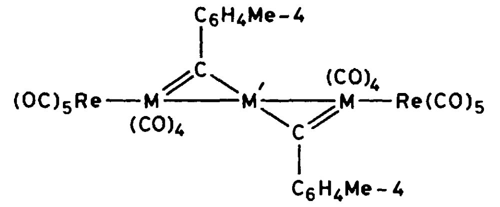
* 2,2,2,2-Tetracarbonyl-2-pentacarbonylrhenio-1,2-μ-*p*-tolylmethylidyne-1,1-bis(trimethylphosphine)platinumtungsten (*Pt–W*)(*Re–W*).

Supplementary data available (No. SUP 56532, 3 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Analytical[a] and physical data for the complexes

Compound[b]	Colour	Yield (%)	$\nu_{max.}(CO)^c/cm^{-1}$	Analysis (%)	
				C	H
(**3a**) $[Re_2Cr_2Pt(\mu\text{-}CR)_2(CO)_{18}]$	Red	62	2 112w (sh), 2 103m, 2 014s, 1 983m (br), 1 885w (br)	29.3 (29.6)	1.1 (1.0)
(**3b**) $[Re_2W_2Pt(\mu\text{-}CR)_2(CO)_{18}]$	Orange	53	[d]2 107w, 2 096s, 2 040w, 2 015vs, 1 990s, 1 982s, 1 942w	24.9 (24.8)	0.9 (0.9)
(**3c**) $[Re_2Cr_2Ni(\mu\text{-}CR)_2(CO)_{18}]$	Brown	60	[e]2 110m, 2 101s, 2 012vs, 1 983m, 1 972m (sh), 1 874w (br), 1 854w (br)	33.2 (32.8)	1.3 (1.1)
(**3d**) $[Re_2W_2Ni(\mu\text{-}CR)_2(CO)_{18}]$	Brown	45	[e]2 105w, 2 094s, 2 040w, 2 013vs, 1 984s, 1 887w (br), 1 867w (br)	27.1 (27.0)	1.0 (0.9)
(**4a**) $[ReWPt(\mu\text{-}CR)(CO)_{10}\{P(C_6H_{11})_3\}]$	Orange	45	2 098s, 2 034s, 1 997vs, 1 968m (sh), 1 917w (br)	35.0 (35.2)	3.3 (3.3)
(**4b**) $[ReCrPt(\mu\text{-}CR)(CO)_9(PMe_3)_2]$[f]	Orange	72	2 092m, 2 000m (sh), 1 992vs, 1 955m		
(**4c**) $[ReWPt(\mu\text{-}CR)(CO)_9(PMe_3)_2]$	Red	83	[d]2 091s, 2 016m, 1 994vs, 1 967s, 1 880w	[g]25.8 (25.3)	2.6 (2.3)
(**5**) $[ReWPt\{\mu\text{-}\sigma{:}\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_9(PMe_3)_2][BF_4]$	Orange	90	2 120s, 2 020vs, 1 993s, 1 959m, 1 802w (br)	23.7 (23.8)	2.2 (2.2)

[a] Calculated values are given in parentheses. [b] R = C_6H_4Me-4. [c] Measured in CH_2Cl_2 unless otherwise stated. [d] In hexane. [e] In thf. [f] Complex unstable, see text, [g] Including $0.5CH_2Cl_2$ of crystallisation.



	M′	M
(**3a**)	Pt	Cr
(**3b**)	Pt	W
(**3c**)	Ni	Cr
(**3d**)	Ni	W

spectrum three signals were observed for CO ligands (Table 2). These peaks could be assigned, on the basis of their chemical shifts, and ^{183}W satellite peaks in the case of (**3b**), to the $M(CO)_4$ (M = Cr or W), radial $Re(CO)_4$, and axial ReCO groups. The observation of only one resonance for the radial carbonyls of the $M(CO)_4$ groups implies a dynamic process involving rotation about an axis through the Cr or W atoms and the mid-points of the μ-C–Pt vectors.

The nickel analogues $[Re_2M_2Ni(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_{18}]$ [(**3c**), M = Cr; (**3d**), M = W] were also prepared from reactions between $[Ni(cod)_2]$ and (**1a**) or (**1c**), respectively, using tetrahydrofuran (thf) as solvent. Data for (**3c**) and (**3d**) are summarised in Tables 1 and 2, and are in accord with the structures proposed.

None of the compounds (**3**) was observed on standing or heating to release CO or metal–carbonyl fragments and afford cluster compounds containing μ_3-CR groups.[3] With this objective in mind the reaction between (**1c**) and $[Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$ was studied in an attempt to obtain a cluster complex containing a μ_3-CReWPt core. It is a well established property of $[Pt(C_2H_4)_2\{P(C_6H_{11})_3\}]$ to abstract CO groups from carbonylmetal complexes, thereby forming cluster compounds incorporating $Pt(CO)\{P(C_6H_{11})_3\}$ fragments.[9] Hence the product of the reaction with (**1c**) might have been a 46-valence-electron metal cluster complex $[ReWPt(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_9\{P(C_6H_{11})_3\}]$, analogous to previously prepared $[FeWPt(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(PEt_3)(\eta\text{-}C_5H_5)]$.[8b] Supporting the hypothesis that (**1c**) might yield a trimetal compound having a μ_3-CReWPt core structure is the nature of its reaction with $[Fe_2(CO)_9]$.[10] The initially formed product is $[ReWFe(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_{13}]$, a species possessing an open Re–W–Fe arrangement; however, CO is readily lost giving $[ReWFe(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_{11}]$.

The compounds (**1c**) and $[Pt(C_2H_4)_2\{P(C_6H_{11})_3\}]$ react at room temperature in light petroleum to give the orange crystalline complex $[ReWPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_{10}\{P(C_6H_{11})_3\}]$ (**4a**). The compound was characterised by the data given in Tables 1 and 2. In the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum, measured at −40 °C, there is a singlet resonance at δ 346.3 p.p.m., with ^{195}Pt satellite peaks [*J*(PtC) 856 Hz], attributable to the ligated carbon of the *C*C_6H_4Me-4 group. The observed chemical shift is in the range expected for the alkylidyne ligand edge-bridging a metal–metal bond.[6] When this group triply bridges a metal triangle the resonance generally occurs in the range 250—300 p.p.m. The non-appearance of any $^{31}P\text{-}^{13}C$ coupling on the signal at 346.3 p.p.m. also suggests that the $\mu\text{-}CC_6H_4Me$-4 and $P(cyclo\text{-}C_6H_{11})_3$ groups are *cis* to one another; an inference supported by the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum discussed below. In the CO region of the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**4a**), peaks due to WCO, ReCO, and PtCO could be identified (Table 2). Moreover, the two resonances due to carbonyl ligands attached to rhenium were characteristic for a radial $Re(CO)_4$ and an axial Re(CO) group. When the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**4a**) was measured at room temperature only two broad CO resonances were observed, indicating that site exchange of the carbonyl groups occurs readily.

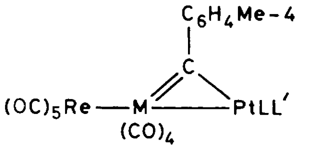
The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum showed a singlet resonance at δ 38.6 p.p.m. with $^{195}Pt\text{-}^{31}P$ coupling (3 496 Hz). The magnitude of this coupling is very similar to those observed in the spectra of the compounds $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(PR_3)(\eta\text{-}C_5H_5)]$ (R = alkyl or aryl) (3 471—3 576 Hz) which also contain $Pt(CO)(PR_3)$ groups with the $\mu\text{-}CC_6H_4Me$-4 and PR_3 groups cisoid.[8a]

Evidently (**4a**) is formed as expected by CO abstraction by platinum, but there is no subsequent formation of a ReWPt

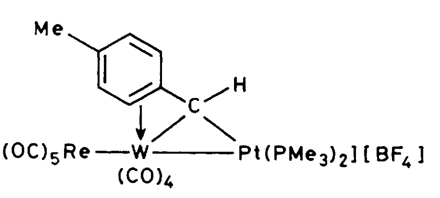
Table 2. Hydrogen-1 and carbon-13 n.m.r. data[a] for the complexes

Compound	^1H (δ)[b]	^{13}C (δ)[c]
(3a)	[d]2.36 (s, 6 H, Me-4), 7.14, 7.62 [$(AB)_2$, 8 H, C_6H_4, J(AB) 8]	331.5 (μ-C), 229.5 [CrCO, J(PtC) 46], 192.0 (8 ReCO), 182.0 (2 ReCO), 149.5 [$C^1(C_6H_4)$], 142.5, 130.0, 129.5 (C_6H_4), 22.0 (Me-4)
(3b)	[d]2.77 (s, 6 H, Me-4), 7.12, 7.61 [$(AB)_2$, 8 H, C_6H_4, J(AB) 8]	298.2 [μ-C, J(PtC) 844, J(WC) 135], 206.9 [WCO, J(PtC) 58, J(WC) 119], 192.9 (8 ReCO), 182.1 (2 ReCO), 149.4 [$C^1(C_6H_4)$, J(PtC) 55], 141.1, 128.9 (C_6H_4), 128.0 [C_6H_4, J(PtC) 9], 20.9 (Me-4)
(3c)	2.28 (s, 6 H, Me-4), 7.09, 7.29 [$(AB)_2$, 8 H, C_6H_4, J(AB) 8]	339.8 (μ-C), 230.7 (CrCO), 192.4 (8 ReCO), 181.3 (2 ReCO), 151.5 [$C^1(C_6H_4)$], 140.3, 128.4, 125.3 (C_6H_4), 20.9 (Me-4)
(3d)[e]	2.22 (s, 6 H, Me-4), 7.08, 7.31 [$(AB)_2$, 8 H, C_6H_4, J(AB) 8]	302.3 (μ-C), 211.1 (WCO), 195.2 (br, ReCO), 153.4 [$C^1(C_6H_4)$], 141.1, 129.7, 125.6 (C_6H_4), 22.3 (Me-4)
(4a)	[d]0.7—2.0 (m, 33 H, C_6H_{11}), 2.35 (s, 3 H, Me-4), 6.68, 7.10 [$(AB)_2$, 4 H, C_6H_4, J(AB) 8]	[f]346.3 [μ-C, J(PtC) 856], 210.5 [WCO, J(WC) 116, J(PtC) 30], 201.0 (4 ReCO), 195.9 (br, PtCO), 187.5 (1 ReCO), 162.0 [$C^1(C_6H_4)$, J(PtC) 64], 135.4, 127.9, 118.3 (C_6H_4), 35.8 [d, $C^1(C_6H_{11})$, J(PC) 21], 29.9—25.5 (C_6H_{11}), 21.3 (Me-4)
(4b)[f]	0.74—1.65 (m, 18 H, MeP), 2.34 (s, 3 H, Me-4), 6.94, 7.10 [$(AB)_2$, 4 H, C_6H_4, J(AB) 8]	389.5 [d, μ-C, J(PC) 62], 234.1 (CrCO), 198.5 (4 ReCO), 186.2 (1 ReCO), 138.9, 135.4, 131.5, 129.5, 128.4, 119.0 (C_6H_4), 21.5 (Me-4), 18.3—17.3 (MeP)
(4c)	1.29 [d, 9 H, MeP, J(PH) 9, J(PtH) 36], 1.69 [d, 9 H, MeP, J(PH) 8, J(PtH) 22], 2.39 (s, 3 H, Me-4), 5.30 (s, 1 H, $0.5CH_2Cl_2$), 6.93, 7.11 [$(AB)_2$, 4 H, C_6H_4, J(AB) 8]	[f]355.2 [d, μ-C, J(PC) 64], 212.3 [WCO, J(WC) 116, J(PtC) 31], 198.2, (4 ReCO), 190.0 (1 ReCO), 164.0 [$C^1(C_6H_4)$], 135.3, 128.3, 118.1 (C_6H_4), 21.3 (Me-4), 19.5—17.7 (MeP)
(5)[g]	[d]1.65 [d, 9 H, MeP, J(PH) 9, J(PtH) 25], 1.79 [d, 9 H, MeP, J(PH) 11, J(PtH) 38], 2.41 (s, 3 H, Me-4), 6.61 [d, 1 H, C_6H_4, J(HH) 6], 7.07—7.25 (m, 4 H, μ-CH and C_6H_4)	213.4 (WCO), 188.4 (4 ReCO), 179.7 (1 ReCO), 144.2, 133.8, 129.0 (C_6H_4), 124.2 [d, μ-C, J(PC) 76, J(PtC) 574], 106.0, 86.7 (C_6H_4), 21.5 (Me-4), 18.7 [d, MeP, J(PC) 37, J(PtC) 44], 15.6 [d, MeP, J(PC) 32, J (PtC) 32]

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. Measurements at room temperature, unless otherwise stated. [b] Measured in $CDCl_3$ unless otherwise stated. [c] Hydrogen-1 decoupled, to high frequency of $SiMe_4$. Measured in CD_2Cl_2–CH_2Cl_2. [d] In CD_2Cl_2. [e] Carbon-13 spectrum measured at −60 °C. [f] Spectra measured at −40 °C. [g] Spectra measured at −20 °C.



	M	L	L
(4a)	W	CO	$P(C_6H_{11})_3$
(4b)	Cr	PMe_3	PMe_3
(4c)	W	PMe_3	PMe_3



(5)

triangle capped by the CC_6H_4Me-4 ligand. Moreover, the reaction is non-stoicheiometric since the product (**4a**) contains $W(CO)_4$ and $Re(CO)_5$ groups, as does the precursor (**1c**). Attempts to convert (**4a**) to a *closo* species with a μ_3-CReWPt core by heating were unsuccessful.

In syntheses related to the preparation of (**4a**), the compounds (**1a**) and (**1c**) underwent reactions with $[Pt(C_2H_4)(PMe_3)_2]$ to give the complexes $[ReMPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_9(PMe_3)_2]$ [(**4b**), M = Cr; (**4c**), M = W], characterised in the usual manner (Tables 1 and 2). The chromium-containing compound (**4b**) was thermally unstable, and microanalytical data could not be obtained. However, the nature of this complex was well established by n.m.r. spectroscopy, measurements being made at −40 °C to avoid decomposition. The ^{13}C-{^1H} n.m.r. spectrum showed resonances due to the μ-C group [δ 389.5 p.p.m., d, J(PC) 62 Hz], and to the CO ligands on chromium (234.1 p.p.m.) and rhenium [198.5 and 186.2 p.p.m. (4:1)]. Interestingly, the C_6H_4 group displayed six distinct resonances, and we comment on this feature later. The ^{31}P-{^1H} spectrum confirmed the presence of the *cis*-$Pt(PMe_3)_2$ group, with doublet signals [J(PP) 15 Hz] at δ −12.2 and −17.7 p.p.m., having ^{195}Pt satellite peaks [J(PtP) 3 950 and 2 690 Hz, respectively]. The larger ^{195}Pt–^{31}P coupling of 3 950 Hz, associated with the resonance at −12.2 p.p.m., is in accord with this signal being due to the PMe_3 ligand transoid to the Pt–W bond.[8]

The ^1H, ^{13}C-{^1H} (Table 2), and ^{31}P-{^1H} data (Experimental section) for (**4c**) are essentially similar to those of (**4b**), and evidently the two compounds are structurally related. Compound (**4c**) was relatively stable and hence could be protonated with $HBF_4 \cdot Et_2O$ to give a salt $[ReWPt\{\mu\text{-}\sigma\text{:}\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_9(PMe_3)_2][BF_4]$ (**5**). The latter is stable as a solid but decomposes in solution above 0 °C. The formulation of this complex, with a σ:η^3-$C(H)C_6H_4Me$-4 bridge system, is based on the precedent of the salt $[PtW\{\mu\text{-}\sigma\text{:}\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)][BF_4]$, the structure of which has been established by *X*-ray diffraction.[11] In the ^1H n.m.r. spectrum of (**5**), measured at −20 °C to avoid decomposition, the peaks for the C_6H_4 group do not appear as an $(AB)_2$ pattern, as in the spectra of compounds (**3**) and (**4**). In contrast there is a doublet signal for one proton at δ 6.61 [J(HH) 6], with a broad multiplet for four others (C_6H_4 and μ-CH) at 7.07—7.25 p.p.m. Similar features are shown by the ^1H n.m.r. spectra of the salts $[PtW\{\mu\text{-}\sigma\text{:}\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}$-

Table 3. Selected internuclear distances (Å) and angles (°) for $[ReWPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_9(PMe_3)_2]\cdot 0.5CH_2Cl_2$ (**4c**) with estimated standard deviations in parentheses

Pt–W	2.771(1)	Pt–P(1)	2.255(6)	P(2)–C(21)	1.857(27)	P(2)–C(22)	1.846(25)
Pt–P(2)	2.346(7)	Pt–C(30)	1.962(23)	P(2)–C(23)	1.827(31)	C(1)–O(1)	1.168(41)
Re–W	3.082(1)	Re–C(1)	1.974(30)	C(2)–O(2)	1.105(35)	C(3)–O(3)	1.162(40)
Re–C(2)	1.980(27)	Re–C(3)	1.971(33)	C(4)–O(4)	1.129(30)	C(5)–O(5)	1.169(37)
Re–C(4)	1.955(25)	Re–C(5)	1.994(28)	C(6)–O(6)	1.183(37)	C(7)–O(7)	1.133(23)
W–C(30)	2.013(24)	W–C(6)	1.999(28)	C(8)–O(8)	1.072(38)	C(9)–O(9)	1.117(23)
W–C(7)	2.029(18)	W–C(8)	2.084(30)	C(10)–Cl(1)	1.422(111)	C(10)–Cl(2)	1.471(84)
W–C(9)	2.021(17)	P(1)–C(11)	1.809(28)	Cl(1)–Cl(2)	2.594(64)		
P(1)–C(12)	1.795(32)	P(1)–C(13)	1.839(28)				

W–Pt–P(1)	146.2(2)	W–Pt–P(2)	115.2(2)	Re–W–C(7)	84.9(6)	C(30)–W–C(7)	106.4(8)
P(1)–Pt–P(2)	98.6(2)	W–Pt–C(30)	46.6(7)	C(6)–W–C(7)	88.7(10)	Pt–W–C(8)	67.8(6)
P(1)–Pt–C(30)	100.0(7)	P(2)–Pt–C(30)	160.1(6)	Re–W–C(8)	86.0(7)	C(30)–W–C(8)	106.4(10)
W–Re–C(1)	83.7(7)	W–Re–C(2)	89.5(10)	C(6)–W–C(8)	167.3(10)	C(7)–W–C(8)	88.7(10)
C(1)–Re–C(2)	87.0(13)	W–Re–C(3)	86.6(7)	Pt–W–C(9)	109.8(6)	Re–W–C(9)	81.9(6)
C(1)–Re–C(3)	170.1(10)	C(2)–Re–C(3)	91.1(13)	C(30)–W–C(9)	86.0(8)	C(6)–W–C(9)	87.2(9)
W–Re–C(4)	175.7(11)	C(1)–Re–C(4)	92.7(11)	C(7)–W–C(9)	166.6(8)	C(8)–W–C(9)	92.5(9)
C(2)–Re–C(4)	92.6(15)	C(3)–Re–C(4)	97.1(12)	Pt–C(30)–W	88.4(11)	Pt–C(30)–C(31)	133.6(14)
W–Re–C(5)	83.4(10)	C(1)–Re–C(5)	90.2(12)	W–C(30)–C(31)	137.4(14)	Re–C(1)–O(1)	174.2(25)
C(2)–Re–C(5)	172.6(13)	C(3)–Re–C(5)	90.4(12)	Re–C(2)–O(2)	174.1(32)	Re–C(3)–O(3)	178.6(17)
C(4)–Re–C(5)	94.4(15)	Pt–W–Re	151.3(1)	Re–C(4)–O(4)	172.0(31)	Re–C(5)–O(5)	173.1(21)
Pt–W–C(30)	45.1(6)	Re–W–C(30)	163.1(6)	W–C(6)–O(6)	175.2(19)	W–C(7)–O(7)	175.6(24)
Pt–W–C(6)	124.1(7)	Re–W–C(6)	81.4(7)	W–C(8)–O(8)	172.9(18)	W–C(9)–O(9)	177.7(23)
C(30)–W–C(6)	86.2(10)	Pt–W–C(7)	83.0(6)				

$(CO)_2(PR_3)_2(\eta\text{-}C_5H_5)][BF_4]$ ($PR_3 = PMe_3$, PMe_2Ph, or $PMePh_2$).[11]

In further support of the structure proposed, there is a signal in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**5**) at δ 124.2 p.p.m., appearing as a doublet [*J*(PC) 76 Hz], with ^{195}Pt satellite peaks [*J*(PtC) 574 Hz] and this resonance can be ascribed to the μ-*C*(H)C_6H_4Me-4 nucleus. In the spectra of the salts $[PtW\{\mu\text{-}\sigma:\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PR_3)_2(\eta\text{-}C_5H_5)][BF_4]$ the corresponding resonances appear in the range 116.3—119.2 p.p.m., with *J*(PC) 74—76 Hz and *J*(PtC) 554—578 Hz. The bridge-bonding mode of the $CH(C_6H_4Me\text{-}4)$ group in (**5**) ensures that the tungsten centre acquires an 18-electron configuration in this salt.

In order to place the structures of the trimetal compounds (**4**) on a firm basis an *X*-ray crystallographic study was carried out on (**4c**), the only one of the three species which provided suitable crystals. The results are summarised in Table 3, and the molecule is shown in Figure 1. As expected, the molecule has a bent Re–W–Pt [151.3(1)°] spine. The Re–W [3.082(1) Å] and W–Pt [2.771(1) Å] separations are close to those found in the related structures $[ReWCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{15}]$ [3.112(1) Å][3] and $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$ [2.751(1) Å].[7] The former contains a pendant $Re(CO)_5$ group, and the latter a bridging tolylmethylidyne ligand as in (**4c**). The alkylidyne carbon C(30) essentially symmetrically bridges the Pt–W bond [C(30)–Pt 1.962(23), C(30)–W 2.013(24) Å], and these distances may be compared with those found in $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$ [μ-C–Pt 1.997(9), μ-C–W 1.967(6) Å].[7]

Transoid to C(30) on the tungsten is the $Re(CO)_5$ group [C(30)–W–Re 163.1(6)°], with the five CO ligands linearly bound to the rhenium so that the latter is in an octahedral environment [mean radial W–Re–C(O) 86, W–Re–C(4) 175(1)°]. The tungsten carries four radially disposed CO groups, and this metal centre is also in an essentially octahedral configuration defined by the W–Re bond, the carbonyl ligands, and the mid-point of the C(30)–Pt vector. The platinum atom is in a close to planar situation, with the angle between the planes defined by P(1)PtP(2) and WPtC(30) being 9.8°. The P–Pt distances are distinctly different [P(1)–Pt 2.255(6), P(2)–Pt 2.346(7) Å], with P(2) being further from the platinum due to the *trans* influence of the alkylidyne group. This feature has been observed in several related structures.[12] The Pt–C(30)–W angle [88.4(11)°] in (**4c**) is very close to that found [87.9(3)°] in $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$.[7]

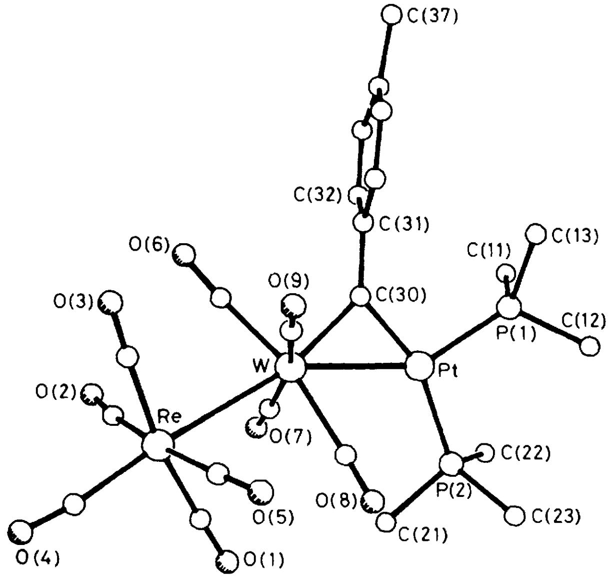


Figure. The molecular structure of $[ReWPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_9(PMe_3)_2]$ (**4c**) showing the atom labelling scheme

As mentioned earlier, the n.m.r. data for (**4b**) and (**4c**) are essentially similar but they differ in one important respect. In the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**4b**) the C_6H_4 group shows six peaks whereas in the spectrum of (**4c**) this group displays four signals (Table 2). The appearance of six resonances in the spectrum of (**4b**) can be understood if in this molecule the C_6H_4 ring lies in the plane of the μ-CWPt ring, a configuration different to that found in the solid-state structure of (**4c**) where the two ring systems are orthogonal, thereby making the pairs

C(32),C(36) and C(33),C(35) chemically equivalent. Therefore, including the resonances due to C(31) and C(34), only four signals would be observed. The spectrum of **(4c)** was measured at −80 °C as well as at −40 °C (Table 2) without any observed change in the pattern. It is possible, therefore, that in solution the C_6H_4Me-4 system is not locked into the position found by *X*-ray diffraction but is undergoing rapid rotation about the C(30)–C(31) bond (Figure) even at −80 °C. This would also lead to the appearance of four n.m.r. signals, due to site exchange of atoms in the two pairs C(32),C(36) and C(33),C(35). A similar rotation mechanism may not be possible for **(4b)** due to steric constraints imposed by the $Cr(CO)_4$ group interacting with the C_6H_4 ring, resulting from a shorter Cr–Pt bond.

Experimental

Light petroleum refers to that fraction of b.p. 40—60 °C. Experiments were carried out using Schlenk-tube techniques, under a dry oxygen-free nitrogen atmosphere. The i.r. spectra were measured with Nicolet MX-10 and MX-5 spectrophotometers and n.m.r. spectra were recorded with JNM JEOL FX 90Q and FX 200 instruments. The compounds $[ReM(\equiv CC_6H_4\text{-}Me\text{-}4)(CO)_9]$ (M = Cr or W) were prepared by the method described for their phenylmethylidyne analogues;[13] $[Pt(C_2H_4)_3]$,[14] $[Pt(C_2H_4)_2\{P(\text{cyclo-}C_6H_{11})_3\}]$,[14] $[Pt(C_2H_4)(PMe_3)_2]$,[7] and $[Ni(cod)_2]$[15] were prepared by methods described earlier. Analytical and other data for the new compounds are given in Table 1. The $^{31}P\text{-}\{^1H\}$ n.m.r. chemical shifts are positive to high frequency of 85% H_3PO_4 (external).

Synthesis of the Compounds $[M'M_2Re_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_{18}]$.—Compounds **(3a)** and **(3b)** were prepared in a similar manner, and therefore, only the synthesis of one compound is described in detail. A light petroleum (20 cm^3) solution of $[Pt(C_2H_4)_3]$ (0.14 mmol) at 0 °C was prepared *in situ* from $[Pt(cod)_2]$.[14] This solution was transferred *via* a canula, using ethylene pressure, into a light petroleum (10 cm^3) solution of **(1c)** (0.20 g, 0.28 mmol) also at 0 °C. The Schlenk-tube was then flushed with nitrogen, and its contents allowed to warm to room temperature. After stirring the mixture for 16 h, solvent was removed *in vacuo* and the residue dissolved in CH_2Cl_2–light petroleum (2 cm^3, 1:1) and chromatographed on a Florisil column (20 × 3 cm). Elution with the same solvent mixture afforded an orange eluate. Removal of solvent *in vacuo* gave orange *microcrystals* of $[Re_2W_2Pt(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_{18}]$ **(3b)** (0.12 g). The compound $[Re_2Cr_2Pt(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_{18}]$ **(3a)** (0.31 g) was obtained from $[Pt(C_2H_4)_3]$ (0.36 mmol) and **(1a)** (0.43 g, 0.72 mmol).

A stirred suspension of $[Ni(cod)_2]$ (0.07 g, 0.24 mmol) in thf (10 cm^3) was treated with **(1c)** (0.30 g, 0.41 mmol) also in thf (10 cm^3). The colour changed immediately from yellow to brown. After 30 min, solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2 (5 cm^3). Florisil (*ca.* 2—3 g) was added to adsorb the product, and after pumping *in vacuo*, all solid material was transferred to the top of a Florisil chromatography column made up with light petroleum. Elution with CH_2Cl_2–light petroleum (3:7) afforded, after removal of solvent, brown *microcrystals* of $[Re_2W_2Ni(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_{18}]$ **(3d)** (0.28 g). Similarly, $[Re_2Cr_2Ni(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_{18}]$ **(3c)** (0.28 g) was obtained from **(1a)** (0.35 g, 0.59 mmol) and $[Ni(cod)_2]$ (0.09 g, 0.32 mmol).

Preparation of the Compound $[ReWPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_{10}\{P(C_6H_{11})_3\}]$.—A light petroleum (10 cm^3) solution of $[Pt(C_2H_4)_2\{P(\text{cyclo-}C_6H_{11})_3\}]$ (0.095 g, 0.15 mmol) was added to a stirred solution of **(1c)** (0.12 g, 0.16 mmol) in the same solvent (10 cm^3). After 4 h, solvent was removed *in vacuo* and the residue dissolved in CH_2Cl_2–light petroleum (2 cm^3, 1:2) and chromatographed on a Florisil column (20 × 3 cm). Elution with the same solvent mixture, and removal of solvent *in vacuo* gave orange *microcrystals* of $[ReWPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_{10}\{P(C_6H_{11})_3\}]$ **(4a)** (0.08 g); $^{31}P\text{-}\{^1H\}$ n.m.r. (in CD_2Cl_2–CH_2Cl_2), δ 38.6 p.p.m. [s, *J*(PtP) 3 496 Hz].

Preparation of the Complexes $[ReMPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_9(PMe_3)_2]$ (M = Cr *or* W).—A suspension of $[Pt(C_2H_4)(PMe_3)_2]$ (0.49 g, 1.30 mmol) in light petroleum (20 cm^3) at 0 °C was added *via* a canula, and under ethylene pressure, to a light petroleum (15 cm^3) solution of **(1c)** (0.94 g, 1.30 mmol) also at 0 °C. After stirring for 30 min, the mixture was cooled to −78 °C and the precipitate which formed was allowed to settle. Solvent was removed with a syringe, and the residue washed with cold (*ca.* −20 °C) light petroleum (3 × 10 cm^3) and dried *in vacuo* affording red *crystals* of $[ReWPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_9(PMe_3)_2]$ **(4c)** (1.16 g); $^{31}P\text{-}\{^1H\}$ n.m.r. (in CD_2Cl_2–CH_2Cl_2), δ −11.1 [d, *J*(PP) 13, *J*(PtP) 4 038] and −21.6 p.p.m. [d, *J*(PP) 13, *J*(PtP) 2 642 Hz].

The thermally sensitive compound $[ReCrPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_9(PMe_3)_2]$ **(4b)** (0.24 g) was similarly prepared from $[Pt(C_2H_4)(PMe_3)_2]$ (0.13 g, 0.35 mmol) and **(1a)** (0.21 g, 0.35 mmol). The product **(4b)** could be handled briefly as a dry solid at room temperature, but solutions rapidly decomposed above *ca.* −20 °C. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum (in CD_2Cl_2–CH_2Cl_2 at −40 °C) of **(4b)** showed resonances at δ −12.2 [d, *J*(PP) 15, *J*(PtP) 3 950] and −17.7 p.p.m. [d, *J*(PP) 15, *J*(PtP) 2 690 Hz].

Protonation of $[ReWPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_9(PMe_3)_2]$.—A diethyl ether (40 cm^3) solution of **(4c)** (0.26 g, 0.24 mmol) at 0 °C was treated with $HBF_4\cdot Et_2O$ (0.2 cm^3). The mixture was stirred for 30 min, producing a pale orange precipitate. Solvent was decanted, and the residue washed with cold (0 °C) diethyl ether (4 × 10 cm^3), and dried *in vacuo* to give orange *microcrystals* of $[ReWPt\{\mu\text{-}\sigma{:}\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_9(PMe_3)_2][BF_4]$ **(5)** (0.28 g); $^{31}P\text{-}\{^1H\}$ n.m.r. (in CD_2Cl_2 at −20 °C), δ −13.5 [d, *J*(PP) 17, *J*(PtP) 2 661] and −17.0 p.p.m. [d, *J*(PP) 17, *J*(PtP) 3 271, *J*(WP) 46 Hz].

Crystal Structure of $[ReWPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_9(PMe_3)_2]$.—Crystals of compound **(4c)** were grown from CH_2Cl_2–light petroleum (1:4). Diffracted intensities were collected on a Nicolet *P*3*m* four-circle diffractometer using a crystal of dimensions *ca.* 0.70 × 0.50 × 0.20 mm. Of the total 4 973 reflections, measured to $2\theta \leqslant 50°$ (ω-scans), 3 815 had $I \geqslant 2.5\sigma(I)$, and only these were used in the refinement of the structure, after the data had been corrected for Lorentz, polarisation, and *X*-ray absorption effects. The latter was by an analytical absorption procedure.[16]

Crystal data. $C_{23}H_{25}O_9P_2PtReW\cdot 0.5CH_2Cl_2$, M = 1 114.5, triclinic, a = 10.624(2), b = 12.073(2), c = 15.135(3) Å, α = 75.97(2), β = 71.52(2), γ = 69.84(1)°, U = 1 708.9(6) Å^3, space group $P\bar{1}$, Z = 2, D_c = 2.17 g cm^{-3}, $F(000)$ = 1 026, Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda}$ = 0.710 69 Å, $\mu(\text{Mo-}K_\alpha)$ = 113.5 cm^{-1}.

The structure was solved by conventional heavy-atom and electron density difference methods. The asymmetric unit was also found to contain a poorly defined molecule of dichloromethane which had a site occupancy of *ca.* 0.5. Hydrogen atoms were not included and all remaining atoms were given anisotropic thermal parameters. Refinement by blocked-cascade least squares converged at *R* 0.075 (*R'* 0.075) with a weighting scheme of the form $w = [\sigma^2(F_o) + 0.000\,8|F_o|^2]^{-1}$ giving a satisfactory weight analysis. A final electron density difference synthesis showed no peaks > 1.1 e Å^{-3} except in the vicinity of the metal atoms where peaks of *ca.* 3 e Å^{-3} were observed. The comparatively poor level of refinement reflects our inability to completely correct for *X*-ray absorption effects,

Table 4. Atomic positional parameters (fractional co-ordinates, × 10^4), with estimated standard deviations in parentheses, for (**4c**)

Atom	x	y	z	Atom	x	y	z
Pt	387(1)	2 479(1)	1 080(1)	O(1)	−593(22)	1 402(18)	4 930(16)
Re	−3 558(1)	2 094(1)	4 601(1)	C(2)	−3 311(29)	384(21)	4 634(26)
W	−1 947(1)	2 249(1)	2 507(1)	O(2)	−3 216(25)	−543(15)	4 588(17)
P(1)	1 274(6)	2 912(5)	−482(4)	C(3)	−5 248(29)	2 559(20)	4 154(19)
P(2)	2 392(6)	2 103(5)	1 579(5)	O(3)	−6 226(21)	2 829(19)	3 873(14)
C(21)	2 413(28)	1 254(22)	2 777(20)	C(4)	−4 473(28)	2 030(31)	5 947(19)
C(22)	3 980(26)	1 165(24)	868(22)	O(4)	−5 137(26)	2 004(29)	6 696(13)
C(23)	2 971(26)	3 368(20)	1 566(21)	C(5)	−3 615(26)	3 802(23)	4 413(26)
C(11)	2 131(39)	1 663(23)	−1 132(19)	O(5)	−3 514(29)	4 770(17)	4 243(19)
C(12)	2 521(29)	3 734(22)	−849(22)	C(6)	−3 186(20)	1 340(19)	2 480(18)
C(13)	121(28)	3 924(21)	−1 211(19)	O(6)	−3 860(19)	786(15)	2 400(14)
C(30)	−1 458(19)	2 463(16)	1 091(16)	C(7)	−620(23)	680(16)	2 923(17)
C(31)	−2 075(18)	2 429(14)	356(14)	O(7)	83(19)	−231(13)	3 133(14)
C(32)	−1 591(25)	1 449(19)	−85(18)	C(8)	−844(22)	3 141(17)	2 856(19)
C(33)	−2 088(27)	1 344(21)	−802(21)	O(8)	−400(18)	3 664(15)	3 081(13)
C(34)	−2 995(23)	2 312(19)	−1 165(17)	C(9)	−3 544(20)	3 744(17)	2 401(16)
C(35)	−3 545(21)	3 311(18)	−676(16)	O(9)	−4 422(19)	4 565(14)	2 313(15)
C(36)	−3 079(21)	3 373(15)	60(16)	C(10)	−54(70)	6 804(88)	3 855(104)
C(37)	−3 458(35)	2 327(26)	−2 017(21)	Cl(1)	−1 307(41)	6 642(36)	3 834(26)
C(1)	−1 692(28)	1 596(24)	4 819(17)	Cl(2)	1 265(45)	5 878(29)	3 903(32)

the presence of ill defined dichloromethane of crystallisation, and the relatively large thermal motion of many of the atoms in the complex. The observed bond length and angle data should therefore be treated with some caution. All computations were carried out on an Eclipse S230 (Data General) computer with the SHELXTL system of programs.[16] Atomic scattering factors were taken from ref. 17. Atomic co-ordinates for (**4c**) are given in Table 4.

Acknowledgements

We thank the S.E.R.C. for support and for the award of a research studentship (to M. J. P.).

References

1 Part 44, S. V. Hoskins, A. P. James, J. C. Jeffery, and F. G. A. Stone, preceding paper.
2 F. G. A. Stone, in 'Inorganic Chemistry: Toward the 21st Century,' ed. M. H. Chisholm, *ACS Symp. Ser.*, 1983, **211**, 383.
3 J. C. Jeffery, D. B. Lewis, G. E. Lewis, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1985, 2001.
4 T. V. Ashworth, M. J. Chetcuti, J. A. K. Howard, F. G. A. Stone, S. J. Wisbey, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1981, 763.
5 N. M. Boag, J. A. K. Howard, M. Green, D. M. Grove, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 2170.
6 J. A. Abad, L. W. Bateman, J. C. Jeffery, K. A. Mead, H. Razay, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1983, 2075.
7 T. V. Ashworth, J. A. K. Howard, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 1609.
8 (*a*) M. J. Chetcuti, K. Marsden, I. Moore, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 1749; (*b*) M. J. Chetcuti, J. A. K. Howard, R. M. Mills, F. G. A. Stone, and P. Woodward, *ibid.*, p. 1757.
9 F. G. A. Stone, *Inorg. Chim. Acta*, 1981, **50**, 33 and refs. therein; *Acc. Chem. Res.*, 1981, **14**, 318.
10 D. G. Evans, J. A. K. Howard, J. C. Jeffery, D. B. Lewis, G. E. Lewis, M. J. Parrott, and F. G. A. Stone, following paper.
11 J. C. Jeffery, J. C. V. Laurie, I. Moore, H. Razay, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1984, 1563.
12 M. R. Awang, J. C. Jeffery, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1983, 2091.
13 E. O. Fischer, T. L. Lindner, F. R. Kreissl, and P. Braunstein, *Chem. Ber.*, 1977, **110**, 3139.
14 J. L. Spencer, *Inorg. Synth.*, 1979, **19**, 213.
15 B. Bogdanović, M. Kröner, and G. Wilke, *Liebigs Ann. Chem.*, 1966, **699**, 1.
16 G. M. Sheldrick, SHELXTL programs for use with the Nicolet *X*-ray system, Cambridge, 1976; updated, Göttingen, 1981.
17 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.

Received 17th October 1985; *Paper* 5/1806