Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 7.[1] Interconversion of Carbene and Carbyne Ligands at a Dimetal Centre. *X*-Ray Crystal Structures of $[CrPt\{\mu\text{-}C(CO_2Me)Ph\}(CO)_4(PMe_3)_3]$ and $[MnPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)][BF_4]\cdot CH_2Cl_2$†

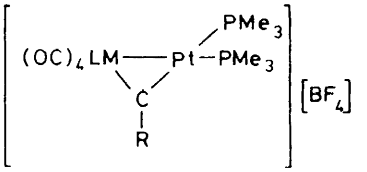
By **Judith A. K. Howard, John C. Jeffery, Mariano Laguna, Rafael Navarro,** and **F. Gordon A. Stone,**
Department of Inorganic Chemistry, The University, Bristol BS8 1TS

Reaction of the dimetal complexes $[MPt\{\mu\text{-}C(OMe)Ph\}(CO)_5(PMe_3)_2]$ with $[OMe_3][BF_4]$ followed by addition of $Li[C_6H_4Me\text{-}4]$ or $Na[OEt]$ afforded the compounds $[MPt\{\mu\text{-}C(Ph)R\}(CO)_5(PMe_3)_2]$ (M = Cr, R = C_6H_4Me-4 or OEt; M = W, R = OEt). Treatment of the compounds $[MPt\{\mu\text{-}C(OMe)R\}(CO)_4(PMe_3)_3]$ (M = Cr, R = Ph; M = W, R = C_6H_4Me-4) with $[OMe_3][BF_4]$ allowed isolation and characterization of the salts $[CrPt(\mu\text{-}CPh)(CO)_4(PMe_3)_3][BF_4]$ and $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMe_3)_3][BF_4]$ respectively. Reaction of $[CrPt(\mu\text{-}CPh)(CO)_4(PMe_3)_3][BF_4]$ with $Na[OMe]$ gave the alkylidene-bridged compound $[CrPt\{\mu\text{-}C(CO_2Me)Ph\}(CO)_4(PMe_3)_3]$, the structure of which was established by *X*-ray diffraction. Crystals are monoclinic, space group $A2/a$, $Z = 8$, in a unit cell with lattice parameters $a = 18.27(3)$, $b = 9.84(1)$, $c = 31.93(5)$ Å, $\beta = 106.2(1)°$. The structure has been refined to R 0.12 (R' 0.12) for 2 292 independent absorption corrected intensities to $2.9 \leqslant 2\theta \leqslant 50°$ (Mo-K_α *X*-radiation) collected at room temperature. The chromium–platinum bond [2.646(7) Å] is bridged by the $\mu\text{-}C(CO_2Me)Ph$ group [C–Pt 1.98(3), C–Cr 2.27(4) Å]. One of the CO ligands is semi-bridging to the platinum [Cr–C–O 157(3)°]. Related platinum–tungsten compounds $[PtW\{\mu\text{-}C(CO_2R)Ph\}(CO)_4(PMe_3)_3]$ (R = Me or Et) have also been prepared. The platinum–manganese and –rhenium compounds $[MPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PR_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (M = Mn, $PR_3 = PMe_3$; M = Re, $PR_3 = PMe_3$ or PMe_2Ph) have been synthesized and an *X*-ray diffraction study made on the manganese compound which crystallises with a molecule of CH_2Cl_2 per molecule of complex in the asymmetric unit. Crystals are monoclinic, space group $P2_1/c$, $Z = 4$, in a unit cell of dimensions $a = 10.434(4)$, $b = 19.334(7)$, $c = 14.901(7)$ Å, and $\beta = 94.42(4)°$. The structure has been refined to R 0.044 (R' 0.046) for 4 223 independent reflections to $2.9 \leqslant 2\theta \leqslant 55°$ (Mo-K_α *X*-radiation) collected at 300 K. In the cation the manganese–platinum bond [2.628(1) Å] is bridged by the CC_6H_4Me-4 group [C–Pt 1.968(8), C–Mn 1.829(8) Å] forming a dimetallacyclopropene ring, the C–Mn separation being indicative of a double bond. The ^1H, ^{31}P, and ^{13}C (^1H decoupled) n.m.r. spectra of the new compounds are reported and discussed.

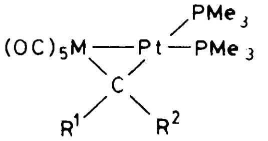
EARLIER we described a general synthesis of heteronuclear dimetal complexes having bridged alkylidene ligands.[1-3] The preparation of these complexes involved attack of a zerovalent metal compound of nickel, palladium, or platinum on a mononuclear metal carbene complex, *e.g.* $[W\{C(OMe)C_6H_4Me\text{-}4\}(CO)_5]$ or $[Mn\{C(OMe)Ph\}(CO)_2(\eta\text{-}C_5H_5)]$. The presence of dimetallacyclopropane ring systems $\overline{M(\mu\text{-}CR^1R^2)M'}$ (M = Cr, Mo, W, or Mn; M' = Ni, Pd, or Pt; R^1 = alkyl or aryl, R^2 = OR or Ph) in these new compounds presages much new chemistry *via* substitution or insertion reactions at the metal centres or at the bridging carbon atoms. Herein we describe some reactions at the carbon atoms of the rings. Our first objective was to create a link between the heteronuclear dimetal compounds having bridging alkylidene ligands[1-3] and those containing an alkylidyne bridge.[4] A preliminary account of this work has been given.[5]

RESULTS AND DISCUSSION

Most of the dimetallacyclopropane ring complexes we have described[1-3] have had an OMe substituent attached to the bridging carbon atom. Removal of this group formally as methoxide ion should convert these compounds into cationic species having dimetallacyclopropene rings and bridging alkylidyne ligands. If such cations are obtained then on treatment with anionic nucleophiles (*e.g.* OR^- or R^-) neutral dimetal compounds with bridging alkylidene groups should be regenerated.



	M	L	R
(1)	Cr	CO	Ph
(4)	W	CO	Ph
(6)	Cr	PMe₃	Ph
(7)	W	PMe₃	C₆H₄Me-4
(10)	Cr	PMe₃	C₆H₄Me-4
(12)	W	PMe₃	Ph



	M	R^1	R^2
(2)	Cr	Ph	C_6H_4Me-4
(3)	Cr	Ph	OEt
(5)	W	Ph	OEt

Initial experiments were carried out with the complex $[CrPt\{\mu\text{-}C(OMe)Ph\}(CO)_5(PMe_3)_2]$.[2] Treatment of a dichloromethane solution of the latter with the reagent $[OMe_3][BF_4]$ apparently afforded the salt (1), since on addition of $Li[C_6H_4Me\text{-}4]$ the orange crystalline complex

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† *defg*-Tetracarbonyl-*c*-μ-methoxycarbonylphenylmethylidene-*abh*-tris(trimethylphosphine)platinumchromium(*Pt–Cr*) and *de*-dicarbonyl-*f*-(η-cyclopentadienyl)-*c*-μ-*p*-tolylmethylidyne-*ab*-bis(trimethylphosphine)platinummanganese(1+) (*Pt–Mn*) tetrafluoroborate–dichloromethane (1/1).

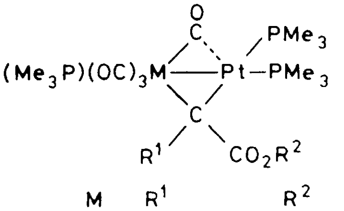
(2) was produced. The neutral compound (2) was characterised by microanalysis (Table 1), and by its ^{1}H and ^{31}P n.m.r. spectra (Table 2). These spectra were in complete accord with the dimetallacyclopropane ring structure proposed, with the metal–metal bond now spanned by a μ-CPh(C_6H_4Me-4) group. Spectra of structurally similar compounds have been discussed previously.[1,2] Formation of (2) occurred in low yield (5—10%), perhaps because of the fragile nature[6] of the starting complex [CrPt{μ-C(OMe)Ph}$(CO)_5(PMe_3)_2$] and the possibility that the nucleophile $(C_6H_4Me\text{-}4)^-$ attacks the salt (1) at centres other than the bridging carbyne-carbon, leading to the formation of by-products. The appearance in the i.r. spectrum of (2) of a ν(CO) band at 1 879 cm^{-1} suggests that one of the carbonyl groups is semi-bridging. However, this might not be so since *X*-ray crystallographic studies on the compounds [WPt{μ-C(OMe)Ph}$(CO)_5(PMe_3)_2$] [2] and [WPt{μ-C(OMe)-C_6H_4Me-4}$(CO)_4(PMe_3)_3$] [1] have revealed an absence of any semi-bridging carbonyl ligand in these species even though in their i.r. spectra CO bands occur at *ca.* 1 850 cm^{-1}.

TABLE 1

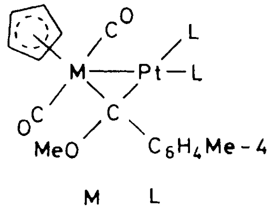
Analytical [a] and physical data for the dimetal complexes

	Compound	M.p. (θ_c/°C)	Colour	Analysis (%)	
				C	H
(2)	$[(OC)_5\overline{Cr\{\mu\text{-}CPh(C_6H_4Me\text{-}4)\}Pt}(PMe_3)_2]$	119—121	Orange	41.2 (41.7)	4.3 (4.2)
(3)	$[(OC)_5\overline{Cr\{\mu\text{-}C(OEt)Ph\}Pt}(PMe_3)_2]$	126—129	Orange	34.6 (35.6)	4.5 (4.2)
(5)	$[(OC)_5\overline{W\{\mu\text{-}C(OEt)Ph\}Pt}(PMe_3)_2]$	129—131 [b]	Orange	29.5 (29.8)	3.7 (3.5)
(6)	$[(Me_3P)(OC)_4\overline{Cr(\mu\text{-}CPh)Pt}(PMe_3)_2][BF_4]$	184—185	Brown	31.0 (31.5)	4.3 (4.2)
(7)	$[(Me_3P)(OC)_4\overline{W(\mu\text{-}CC_6H_4Me\text{-}4)Pt}(PMe_3)_2][BF_4]$	135—137 [b]	Green	27.5 (27.7)	3.8 (3.8)
(8)	$[(Me_3P)(OC)_4\overline{Cr\{\mu\text{-}C(CO_2Me)Ph\}Pt}(PMe_3)_2]$	159—161	Yellow	35.6 (35.9)	4.9 (4.8)
(9)	$[(Me_3P)(OC)_4\overline{Cr\{\mu\text{-}C(CO_2Et)Ph\}Pt}(PMe_3)_2]$	140—141	Yellow	36.9 (36.7)	5.0 (5.0)
(11)	$[(Me_3P)(OC)_4\overline{Cr\{\mu\text{-}C(CO_2Me)C_6H_4Me\text{-}4\}Pt}(PMe_3)_2]$	130 [b]	Yellow	37.3 (36.9)	5.3 (5.0)
(13)	$[(Me_3P)(OC)_4\overline{W\{\mu\text{-}C(CO_2Me)Ph\}Pt}(PMe_3)_2]$	160—162	Yellow	30.2 (30.5)	4.1 (4.1)
(14)	$[(Me_3P)_2(OC)_3\overline{W\{\mu\text{-}C(CO_2Me)Ph\}Pt}(PMe_3)_2]$	159—161	Yellow	31.9 (31.5)	5.2 (4.8)
(15)	$[(Me_3P)(OC)_4\overline{W\{\mu\text{-}C(CO_2Et)Ph\}Pt}(PMe_3)_2]$	134—135	Yellow	31.0 (31.3)	4.2 (4.2)
(16)	$[(\eta\text{-}C_5H_5)(OC)_2\overline{Mn\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt}(PMe_3)_2]$	150—156 [b]	Yellow	40.1 (40.2)	5.2 (5.1)
(17)	$[(\eta\text{-}C_5H_5)(OC)_2\overline{Mn(\mu\text{-}CC_6H_4Me\text{-}4)Pt}(PMe_3)_2][BF_4]$ [c]	72—80 [b]	Purple	32.0 (31.6)	4.1 (4.0)
(18)	$[(\eta\text{-}C_5H_5)(OC)_2\overline{Re\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt}(PMe_3)_2]$	116—120 [b]	Yellow	33.7 (33.5)	4.2 (4.4)
(19)	$[(\eta\text{-}C_5H_5)(OC)_2\overline{Re(\mu\text{-}CC_6H_4Me\text{-}4)Pt}(PMe_3)_2][BF_4]$	75—78 [b]	Dark red	29.6 (29.8)	3.9 (3.6)
(20)	$[(\eta\text{-}C_5H_5)(OC)_2\overline{Re\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt}(PMe_2Ph)_2]$	130—132 [b]	Yellow	42.0 (42.1)	4.4 (4.1)
(21)	$[(\eta\text{-}C_5H_5)(OC)_2\overline{Re(\mu\text{-}CC_6H_4Me\text{-}4)Pt}(PMe_2Ph)_2][BF_4]$	65 [b]	Red	37.9 (38.4)	3.7 (3.5)

[a] Calculated values are given in parentheses. [b] With decomposition. [c] CH_2Cl_2 solvate, see *X*-ray data.



	M	R^1	R^2
(8)	Cr	Ph	Me
(9)	Cr	Ph	Et
(11)	Cr	C_6H_4Me-4	Me
(13)	W	Ph	Me
(15)	W	Ph	Et



	M	L
(16)	Mn	PMe_3
(18)	Re	PMe_3
(20)	Re	PMe_2Ph

Reaction of [CrPt{μ-C(OMe)Ph}$(CO)_5(PMe_3)_2$] with $[OMe_3][BF_4]$ followed by addition of Na[OEt] in ethanol gave the orange compound (3) with a bridging μ-C(OEt)-Ph group. The ^{1}H and ^{31}P n.m.r. spectra (Table 2) are in accord with the anticipated structure. The overall yield of (3) from [CrPt{μ-C(OMe)Ph}$(CO)_5$-$(PMe_3)_2$] was also low. Hence attention was next directed at analogous reactions of the tungsten compound [PtW{μ-C(OMe)Ph}$(CO)_5(PMe_3)_2$],[2] which afforded *via* the presumed salt (4) the neutral compound (5), using a similar sequence of reactions to those which gave (3). Although yields of (5) were double those of (3) they were relatively low, and there was again evidence of side reactions.

In view of these results it was thought important to isolate some of the intermediate salts. It had been found previously[1] that the stability of complexes containing the ring system $\overline{M(\mu\text{-}CR^1R^2)Pt}$ (M = Cr or W) is considerably enhanced if one of the five carbonyl groups attached to chromium or tungsten is replaced by a tertiary phosphine group. Hence, in an attempt to isolate a salt containing a bridging alkylidyne ligand, the complex $[CrPt\{\mu\text{-}C(OMe)Ph\}(CO)_4(PMe_3)_3]$ [2] was treated with $[OMe_3][BF_4]$ in dichloromethane, giving orange-brown microcrystals identified as the desired product (6) (Table 1). The CO stretching bands in the i.r. spectra of (6) were shifted to higher frequency than those observed [2] in the spectrum of the precursor, as expected for a cationic species, but one band at 1 833 cm^{-1} was perhaps suggestive of a semi-bridging CO ligand or even of an alternative structure (see later).

The ^{31}P n.m.r. spectrum of (6) showed three resonances (Table 2), one of which is clearly assignable to a $CrPMe_3$ group on account of the small *J*(PtP) coupling, and the chemical shift. The ^{1}H spectrum was as expected, and no signal for an OMe group, present in the spectrum of the precursor $[CrPt\{\mu\text{-}C(OMe)Ph\}(CO)_4(PMe_3)_3]$, was observed. Moreover, the salt (6) could be readily obtained in reasonable yield, and seemed always to be formed as a single isomer as deduced from the spectroscopic properties.

TABLE 2

Phosphorus-31 and ^{1}H n.m.r. data [a] for the platinum–chromium and –tungsten compounds

	Complex	^{31}P (δ/p.p.m.) [b]	^{1}H (τ)
(2)	$[CrPt\{\mu\text{-}CPh(C_6H_4Me\text{-}4)\}(CO)_5(PMe_3)_2]$ [c]	16.0 [d, *J*(PP) 8, *J*(PtP) 2 465], 23.4 [d, *J*(PP) 8, *J*(PtP) 4 582]	2.2—3.2 (m, 9 H, Ph, C_6H_4), 6.87 (s, 3 H, Me-4), 8.41 [d, 9 H, MeP, *J*(PH) 8, *J*(PtH) 21], 8.66 [d, 4 H, MeP, *J*(PH) 10, *J*(PtH) 45]
(3)	$[CrPt\{\mu\text{-}C(OEt)Ph\}(CO)_5(PMe_3)_2]$	14.6 [d, *J*(PP) 5, *J*(PtP) 2 444], 22.3 [d, *J*(PP) 5, *J*(PtP) 4 527]	2.4—3.3 (m, 5 H, Ph), 6.21 [q, 2 H, CH_2, *J*(HH) 7], 8.36 [d, 9 H, MeP *J*(PH) 7, *J*(PtH) 19], 8.66 [d, 9 H, MeP, *J*(PH) 11, *J*(PtH) 45], 8.69 [t, 3 H, CH$_2$*Me*, *J*(HH) 7]
(5)	$[PtW\{\mu\text{-}C(OEt)Ph\}(CO)_5(PMe_3)_2]$	15.3 [d, *J*(PP) 11, *J*(PtP) 2 510], 22.4 [d, *J*(PP) 11, *J*(PtP) 4 490]	2.48—3.18 (m, 5 H, Ph), 6.23 [q, 2 H, CH_2, *J*(HH) 8], 8.36 [d, 9 H, MeP, *J*(PH) 8, *J*(PtH) 22], 8.69 [d, 9 H, MeP, *J*(PH) 11, *J*(PtH) 45], 8.60 [t, 3 H, CH$_2$*Me*, *J*(HH) 8]
(6)	$[CrPt(\mu\text{-}CPh)(CO)_4(PMe_3)_3][BF_4]$	−3.8 [s, PCr, *J*(PtP) 51], 7.1 [d, PPt, *J*(PP) 31, *J*(PtP) 3 386], 10.6 [d, PPt, *J*(PP) 31, *J*(PtP) 3 042]	2.8 (m, 5 H, Ph), 8.04 [d, 9 H, MeP, *J*(PH) 11], 8.22 [d, 9 H, MeP, *J*(PH) 12], 8.42 [d, 9 H, MeP, *J*(PH) 9]
(7)	$[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMe_3)_3][BF_4]$ [d]	6.5 [d of d, PPt, *J*(PP) 10 and 3, *J*(PtP) 4 238], 20.6 [d, PPt, *J*(PP) 3, *J*(PtP) 2 529], 43.3 [d, PW, *J*(PP) 10, *J*(WP) 164, *J*(PtP) 27]	2.8—3.1 (m, 4 H, C_6H_4), 7.60 (s, 3 H, C$_6$H$_4$*Me*), 8.10 [d, 9 H, MePW, *J*(PH) 9], 8.27 [d, 9 H, MePPt, *J*(PH) 9, *J*(PtH) 23], 8.61 [d, 9 H, MePPt, *J*(PH) 10, *J*(PtH) 42]
(8)	$[CrPt\{\mu\text{-}C(CO_2Me)Ph\}(CO)_4(PMe_3)_3]$ [e]	−4.5 [t, PCr, *J*(PP) 9, *J*(PPt) 59], 16.2 [d, PPt, *J*(PP) 9 and 15, *J*(PPt) 4 327 and 2 413]	2.1—3.0 (m, 5 H, Ph), 6.42 (s, OMe), 8.33 [d, 9 H, MePPt, *J*(PH) 8, *J*(PtH) 20], 8.61 [d, 9 H, MePPt, *J*(PH) 10, *J*(PtH) 40], 8.73 [d, 9 H, MePCr, *J*(PH) 9]
(9)	$[CrPt\{\mu\text{-}C(CO_2Et)Ph\}(CO)_4(PMe_3)_3]$	−4.3 [d, PCr, *J*(PP) 8, *J*(PtP) 56], 16.3 [d, PPt, *J*(PP) 15, *J*(PtP) 2 405], 17.0 [d of d, PPt, *J*(PP) 15 and 8, *J*(PtP) 4 377]	2.1—3.3 (m, 5 H, Ph), 5.95 [q, 2 H, CH_2, *J*(HH) 7], 8.32 [d, 9 H, MePPt, *J*(PH) 8, *J*(PtH) 20], 8.58 [d, 9 H, MePPt, *J*(PH) 11, *J*(PtH) 40], 8.75 [d, 9 H, MePCr, *J*(PH) 8], 8.76 [t, 3 H, CH$_2$*Me*, *J*(HH) 7]
(11)	$[CrPt\{\mu\text{-}C(CO_2Me)C_6H_4Me\text{-}4\}(CO)_4(PMe_3)_3]$ [e]	−4.6 [t, PCr, *J*(PP) 9, *J*(PtP) 57], 16.3 [d, PPt, *J*(PP) 9 and 15, *J*(PPt) 4 353 and 2 411]	2.28—3.20 (m, 4 H, C_6H_4), 6.46 (s, 3 H, OMe), 7.82 (s, 3 H, Me-4), 8.34 [d, 9 H, MePPt, *J*(PH) 8, *J*(PtH) 18], 8.53 [d, 9 H, MePPt, *J*(PH) 10, *J*(PtH) 40], 8.75 [d, 9 H, MePW, *J*(PH) 8]
(13)	$[PtW\{\mu\text{-}C(CO_2Me)Ph\}(CO)_4(PMe_3)_3]$	17.7 [d of d, PPt, *J*(PP) 16 and 2, *J*(PPt) 2 547], 20.6 [d of d, PPt, *J*(PP) 16 and 14, *J*(PW) 17, *J*(PPt) 4 322], 40.9 [d of d, PW, *J*(PP) 14 and 2, *J*(PW) 232, *J*(PPt) 34]	2.05—3.30 (m, 5 H, Ph), 6.43 (s, 3 H, OMe), 8.30 [d, 9 H, MePPt, *J*(PH) 9, *J*(PtH) 22], 8.54 [d, 9 H, MePW, *J*(PH) 8], 8.60 [d, 9 H, MePPt, *J*(PH) 10, *J*(PtH) 40]
(14)	$[PtW\{\mu\text{-}C(CO_2Me)Ph\}(CO)_3(PMe_3)_4]$ [f]	16.8 [d of d, PPt, *J*(PP) 15 and 4, *J*(PPt) 2 482], 22.5 [d of d, PPt, *J*(PP) 15 and 5, *J*(PPt) 4 300], 40.6 [d of d, PW, *J*(PP) 32 and 4, *J*(PW) 150], 43.1 [d of d, PW, *J*(PP) 32 and 5, *J*(PW) 133, *J*(PPt) 85]	1.66—3.20 (m, 5 H, Ph), 6.40 (s, 3 H, OMe), 8.63 [d, 9 H, MePW, *J*(PH) 8], 8.64 [d, 9 H, MePPt, *J*(PH) 9, *J*(PtH) 20], 8.93 [d, 9 H, MePPt, *J*(PH) 9, *J*(PtH) 38], 9.14 [d, 9 H, MePW, *J*(PH) 7]
(15)	$[PtW\{\mu\text{-}C(CO_2Et)Ph\}(CO)_4(PMe_3)_3]$	17.7 [d, PPt, *J*(PP) 16, *J*(PPt) 2 535], 21.3 [d of d, PPt, *J*(PP) 16 and 13, *J*(PPt) 4 368], 40.7 [d, PW, *J*(PP) 13, *J*(PW) 217, *J*(PPt) 52]	2.07—3.33 (m, 5 H, Ph), 5.99 [q, 2 H, CH_2, *J*(HH) 7], 8.34 [d, 9 H, MePPt, *J*(PH) 8, *J*(PtH) 20], 8.59 [d, 9 H, MePW, *J*(PH) 9], 8.61 [d, 9 H, MePPt, *J*(PH) 11, *J*(PtH) 46], 8.77 [t, 3 H, CH$_2$*Me*, *J*(HH) 7]

[a] Measured in $CDCl_3$ at room temperature unless otherwise stated. Coupling constants in Hz. [b] Hydrogen-1 decoupled, chemical shifts in p.p.m to low frequency of 85% H_3PO_4 (external). [c] ^{31}P in C_6D_6. [d] ^{31}P at −60 °C. [e] Due to the identical chemical shifts in the ^{31}P spectrum of the two *P*Pt groups, the signals are second order and coupling constants are derived from the ^{31}P satellites. [f] ^{1}H in C_6D_6.

The salt (7) was obtained by treating $[PtW\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}(CO)_4(PMe_3)_3]$ with $[OMe_3][BF_4]$. The ^{31}P n.m.r. spectrum (Table 2) showed the expected three resonances, the ^{185}W satellites [J(WP) 164 Hz] on the resonance at δ 43.3 p.p.m. clearly identifying the $WPMe_3$ group. The signals for the non-equivalent PMe_3 groups on Pt showed the usual large ^{195}Pt–^{31}P coupling.[1,2] Unfortunately, no crystals of (6) or (7) were obtained of suitable quality for an *X*-ray diffraction study. Hence the structures depicted for the cations have not been fully confirmed, which is unfortunate in view of the unusual nature of the reactions with alkoxide ions about to be described.

The salt (6) was treated with sodium methoxide in methanol in the expectation that the bridged carbene complex $[CrPt\{\mu\text{-}C(OMe)Ph\}(CO)_4(PMe_3)_3]$ would be regenerated. However, reaction occurred to give a new bright yellow compound (8), the i.r. spectrum of which, in addition to showing four strong bands due to CO ligands (see Experimental section), unexpectedly had a band at 1 626 cm^{-1}. The ^{31}P n.m.r. spectrum of (8) showed a resonance at δ —4.5 p.p.m. assignable to a $CrPMe_3$ group, and a complex resonance at 16.2 p.p.m. due to the PMe_3 groups attached to platinum. Evidently the latter ligands give rise to resonances with identical shifts; the signals are second order and coupling constants (Table 2) were derived from the ^{195}Pt satellites. The ^1H spectrum showed the expected resonances for Ph, Me, and OMe groups.

Sodium ethoxide reacted with (6) to give a similar product (9) which also had a band in the region 1 600—1 650 cm^{-1}. The three resonances in the ^{31}P n.m.r. spectrum identified the $CrPMe_3$ and *cis*-$Pt(PMe_3)_2$ groups, and the ^1H spectrum showed all the signals for addition of OEt^- to (6).

Another dimetal complex (11), similar in nature to (8) and (9), was prepared by treating the *in situ* generated salt (10) with methoxide ion. This compound (11) [$\nu_{max.}$ 1 625 cm^{-1}] was characterised in a similar manner (Tables 1 and 2). Treatment of the platinum–tungsten salt (12), prepared *in situ* from $[PtW\{\mu\text{-}C(OMe)Ph\}(CO)_4(PMe_3)_3]^2$ and $[OMe_3][BF_4]$, with OMe^- yielded a mixture which after chromatography gave the crystalline compounds (13) and (14). Compound (13) proved to be the tungsten analogue of the chromium complex (8). However, examination of the ^{31}P n.m.r. spectrum of (14) (Table 2) revealed the presence of four PMe_3 ligands, two of which were bonded to platinum and two to the tungsten. Both (13) and (14) showed a band near 1 620 cm^{-1} in their i.r. spectra. Reaction of the salt (12) with sodium ethoxide gave a compound (15), analogous to the chromium compound (9).

The presence of bands in the range 1 600—1 650 cm^{-1} in the i.r. spectra of the compounds (8), (9), (11), (13), and (15) is consistent with several possible structures. Thus, metal-bridging carbonyls give rise to a band at such a low frequency when they behave as four-electron donors as in $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ (dppm = $Ph_2PCH_2PPh_2$) [ν(CO), 1 645 cm^{-1}] [7] or exhibit a dimetallated ketone structure as in $[Pt_2Cl_2(\mu\text{-}CO)(\mu\text{-}dpam)](dpam = Ph_2AsCH_2AsPh_2)$ [ν(CO), 1 635 cm^{-1}].[8] Neither of these modes of bonding seemed likely in the compounds in question. It seemed more probable that the bands at *ca.* 1 620 cm^{-1} were due to the presence in these molecules of a metal–metal bond bridged by either a $C(OR^2)(R^1)C(O)$ or a $C(CO_2R^2)(R^1)$ group. Either of these systems might arise during attack of alkoxide ion on the alkylidyne salts if a CO ligand on the chromium or tungsten atoms became involved in the process. Hence in order to elucidate the true nature of the bridging organic ligand in the compounds (8), (9), (11), (13), and (15), it became essential to carry out an *X*-ray crystallographic study. For this work it was difficult to obtain suitable crystals but, although small and plate-like, a crystal of (8) was studied.

The results of the *X*-ray diffraction study are summarised in Tables 3—5, and the molecular structure with the atomic numbering scheme is shown in Figure 1. It is immediately apparent that the chromium–platinum bond is bridged by a $C(CO_2Me)Ph$ group, and thus the i.r. band shown by this compound at 1 626 cm^{-1} is due to the C=O absorption. A similar carboalkoxy-bridge system in the related compounds (9), (11), (13), and (15) would account for the corresponding bands in the i.r. spectra of these complexes. The $C(CO_2Me)Ph$ ligand in (8) asymmetrically bridges the metal–metal bond. The Pt–C(5) distance [1.98(3) Å] is at the short end of the range [1.99(3)—2.15(2) Å] generally observed for

TABLE 3

Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses for complex (8)

Atom	*x*	*y*	*z*
Pt	0.172 0(1)	0.218 4(2)	0.106 8(1)
Cr	0.136 0(4)	0.413 6(7)	0.154 6(2)
P(1)	0.296 9(7)	0.232 7(14)	0.103 3(4)
C(11)	0.354(4)	0.082(7)	0.110(2)
C(12)	0.315(4)	0.280(7)	0.055(2)
C(13)	0.353(3)	0.345(6)	0.147(2)
P(2)	0.143 4(8)	0.012 4(12)	0.075 9(4)
C(21)	0.044(3)	−0.037(5)	0.064(2)
C(22)	0.186(3)	−0.136(6)	0.106(2)
C(23)	0.159(3)	−0.003(5)	0.023(1)
P(3)	0.080 0(7)	0.449 5(12)	0.211 7(3)
C(31)	0.131(3)	0.391(5)	0.264(1)
C(32)	−0.018(3)	0.393(5)	0.210(2)
C(33)	0.067(3)	0.627(5)	0.222(2)
C(1)	0.173(3)	0.441(4)	0.110(1)
O(1)	0.201(2)	0.511(3)	0.083(1)
C(2)	0.204(2)	0.553(4)	0.177(1)
O(2)	0.246(2)	0.640(4)	0.190(1)
C(3)	0.060(3)	0.531(4)	0.124(1)
O(3)	0.019(2)	0.609(3)	0.104(1)
C(4)	0.212(3)	0.301(5)	0.193(1)
O(4)	0.253(2)	0.240(3)	0.218(1)
C(5)	0.074(2)	0.226(4)	0.121(1)
O(5)	0.126(2)	0.062(3)	0.172(1)
C(6)	0.057(2)	0.130(4)	0.154(1)
O(6)	0.003(2)	0.102(4)	0.165(1)
C(7)	0.124(3)	−0.023(6)	0.208(2)
C(41)	−0.004(1)	0.270(3)	0.087(1)
C(42)	−0.076(1)	0.270(3)	0.094(1)
C(43)	−0.140(1)	0.314(3)	0.061(1)
C(44)	−0.131(1)	0.356(3)	0.021(1)
C(45)	−0.059(1)	0.356(3)	0.014(1)
C(46)	0.004(1)	0.312(3)	0.047(1)

platinum(II)–carbon(sp^3) σ bonds,[9] and compares with 2.02(1) and 2.04(1) Å found for the corresponding Pt–μ-C distances in [PtW{μ-C(OMe)C_6H_4Me-4}$(CO)_4(PMe_3)_3$] [1] and [PtW{μ-C(OMe)Ph}$(CO)_5(PMe_3)_2$],[2] respectively.

In spite of the covalent radius of chromium (1.18 Å) being less than that of platinum (1.30 Å) or tungsten (1.30 Å), chromium(II)–carbon(sp^3) σ bonds are as long (2.15—2.29 Å) [10] as their platinum or tungsten counterparts. The Cr–C(5) separation [2.27(4) Å] in compound (8) is thus typical of that observed for such bonds in other formally chromium(II) complexes. In [{Cr(CH_2SiMe_3)(μ-CH_2SiMe_3)(PMe_3)}$_2$] the Cr–μ-C distances are 2.18 and 2.27 Å, the asymmetry in the bridge system being attributed to steric effects of the bulky ligands.[11]

TABLE 4

Bond lengths (Å) and angles (°) for the complex [CrPt{μ-C(CO_2Me)Ph}$(CO)_4(PMe_3)_3$] (8)

(*a*) Distances			
Cr–Pt	2.646(7)	Pt–C(5)	1.98(3)
Pt–P(1)	2.32(1)	Cr–C(5)	2.27(4)
Pt–P(2)	2.25(1)	Cr–C(1)	1.75(5)
Cr–P(3)	2.35(2)	Pt–P(1)	2.19(4)
		Pt · · · O(5)	2.90(4)
P(1)–C(11)	1.79(6)	Cr–C(2)	1.85(4)
P(1)–C(12)	1.74(6)	C(2)–O(2)	1.16(5)
P(1)–C(13)	1.85(6)	Cr–C(3)	1.86(5)
P(2)–C(21)	1.81(5)	C(3)–O(3)	1.13(5)
P(2)–C(22)	1.80(6)	Cr–C(4)	1.93(5)
P(2)–C(23)	1.79(5)	C(4)–O(4)	1.10(5)
P(3)–C(31)	1.77(5)	C(1)–O(1)	1.31(5)
P(3)–C(32)	1.86(5)	C(5)–C(6)	1.49(5)
P(3)–C(33)	1.80(5)	C(6)–O(5)	1.40(5)
C(41)–C(42)	1.39 *	C(6)–O(6)	1.18(5)
C(42)–C(43)	1.39	O(5)–C(7)	1.42(6)
C(43)–C(44)	1.39	C(5)–C(41)	1.60(4)
C(44)–C(45)	1.39		
C(45)–C(46)	1.39		
C(46)–C(41)	1.39		
(*b*) Angles			
P(1)–Pt–P(2)	98.3(5)	C(1)–Cr–C(5)	90(2)
P(1)–Pt–C(5)	168(1)	C(1)–Cr–C(2)	80(2)
P(2)–Pt–C(5)	91(1)	C(1)–Cr–C(3)	83(2)
P(1)–Pt–C(1)	87(1)	C(1)–Cr–C(4)	104(2)
P(2)–Pt–C(1)	157(1)	C(1)–Cr–Pt	55(1)
C(1)–Pt–C(5)	87(2)	P(3)–Cr–C(1)	162(1)
P(1)–Pt–Cr	112.9(4)	P(3)–Cr–C(5)	102(1)
P(2)–Pt–Cr	143.7(4)	P(3)–Cr–Pt	141.9(4)
C(1)–Pt–Cr	41(1)	P(3)–Cr–C(4)	89(1)
C(5)–Pt–Cr	56(1)	P(3)–Cr–C(2)	88(1)
		P(3)–Cr–C(3)	84(1)
		Pt–Cr–C(3)	115(1)
Pt–C(1)–O(1)	120(3)	Cr–C(1)–O(1)	157(3)
Pt–C(1)–Cr	84(2)	Pt–C(5)–Cr	77(1)
Pt–C(5)–C(6)	120(3)	Cr–C(5)–C(6)	110(2)
Pt–C(5)–C(41)	123(2)	Cr–C(5)–C(41)	110(2)
		Cr–C(2)–O(2)	178(4)
Pt–P(1)–C(11)	119(2)	Cr–C(3)–O(3)	174(4)
Pt–P(1)–C(12)	119(2)	Cr–C(4)–O(4)	174(4)
Pt–P(1)–C(13)	110(2)	Cr–P(3)–C(31)	117(2)
Pt–P(2)–C(21)	115(2)	Cr–P(3)–C(32)	124(2)
Pt–P(2)–C(22)	119(2)	Cr–P(3)–C(33)	112(2)
Pt–P(2)–C(23)	115(2)	C(31)–P(3)–C(32)	100(2)
C(11)–P(1)–C(12)	94(3)	C(31)–P(3)–C(33)	102(2)
C(11)–P(1)–C(13)	103(3)	C(32)–P(3)–C(33)	97(3)
C(13)–P(1)–C(12)	108(3)	C(5)–C(6)–O(5)	106(3)
		O(5)–C(6)–O(6)	119(4)
C(21)–P(2)–C(22)	99(2)	C(5)–C(6)–O(6)	135(4)
C(21)–P(2)–C(23)	101(2)	C(6)–O(5)–C(7)	114(4)
C(22)–P(2)–C(23)	105(2)	C(41)–C(5)–C(6)	110(3)

* Parameters not refined, no estimated standard deviation.

In complex (8) the 'asymmetry' of C(5) with respect to chromium and platinum seems only to reflect normal separation for these atoms, unlike the situation in [PtW{μ-C(OMe)Ph}$(CO)_5(PMe_3)_2$] where the W–μ-C distance [2.48(1) Å] [2] is significantly longer than normal (2.14—2.34 Å) tungsten–carbon σ-bond distances.[12]

TABLE 5

Some least-squares planes [a] for the complex [CrPt{μ-C(CO_2Me)Ph}$(CO)_4(PMe_3)_3$] (8)

Plane (*i*): Pt, Cr, C(5)

$$3.06x - 5.28y + 23.87z = 1.92$$

Plane (*ii*): Pt, Cr, C(1)

$$14.41x - 0.24y + 11.83z = 3.69$$

Plane (*iii*): C(5), C(6), C(41)

$$-4.64x + 7.60y + 20.09z = 3.81$$

Plane (*iv*): C(41), C(42), C(43), C(44), C(45), C(46)

$$1.06x + 9.21y + 10.11z = 3.36$$

Plane (*v*): Pt, P(1), P(2)

$$1.24x - 4.22y + 27.02z = 2.18$$

Plane (*vi*) [b]: P(3), Cr, C(1), C(3), C(4)

$$8.76x + 7.82y + 7.10z = 5.63$$

[P(3) 0.09, Cr −0.10, C(1) 0.12, C(3) −0.07, C(4) −0.04]

Dihedral angles (°) between planes

	(ii)	(iii)	(v)	(vi)
(i)	49	89	9	92

[a] *x*, *y*, *z* are fractional crystal co-ordinates. [b] Distances of atoms from plane given in square brackets.

Unlike the two tungsten–platinum complexes with bridging μ-C(OMe)R (R = Ph or C_6H_4Me-4) ligands, referred to above, compound (8) has a semi-bridging carbonyl group. The angle Cr–C(1)–O(1) of 157(4)° lies half-way between that for a linear M–C–O group and that in a structure with a symmetric $\overline{\text{M–}\mu\text{-CO–M}}$ bridge.[13] It is proposed that this behaviour reflects back-bonding from the platinum into the π^* orbital of this CO ligand so as to reduce electron density on the platinum, which could be electron rich due to donation of σ electron density from the PMe_3 groups and the carbene ligand.

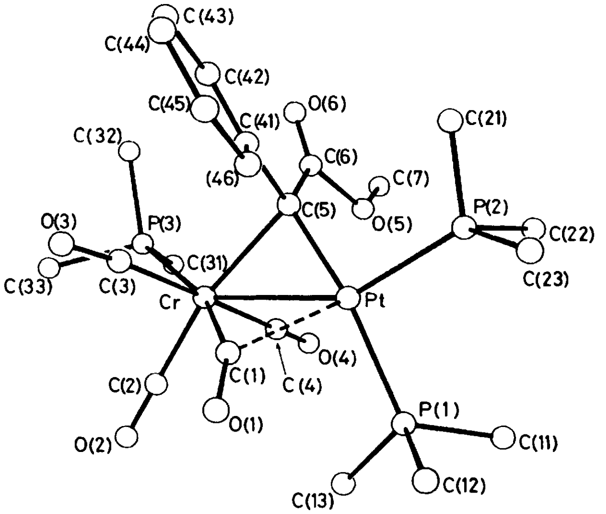


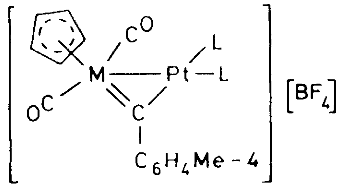
FIGURE 1 'Ball and stick' diagram showing the molecular structure and atom-numbering scheme for [CrPt{μ-C(CO_2Me)Ph}$(CO)_4(PMe_3)_3$]

This would be relieved by charge transfer to the CO group. The semi-bridging carbonyl thus exists to disperse excess of charge at one metal centre as in $[CoFe(CO)_8]^-$ (ref. 14).

In compound (8) the angle between the two planes defined by Cr–Pt–C(5) and C(6),C(5),C(41) is 89° which compares with 87.3° for the two corresponding planes in $[PtW\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}(CO)_4(PMe_3)_3]$.[1] The angle Cr–C(5)–Pt is 77(1)°, and this may be compared with 79.4° found for the Pt–μ-C–W angle in the aforementioned tungsten species. As previously found in this type of alkylidene bridge compound,[1] the platinum atom is in an essentially planar environment, since the planes defined by P(1)–Pt–P(2) and Cr–C(5)–Pt are inclined by only 9° to each other (Table 5). The angles P(1)–Pt–P(2) and P(2)–Pt–C(5) are 98.3(5)° and 91(1)°, respectively, so that P(1) is *trans* to C(5). The geometry about the chromium atom is such that several of the angles subtended at the metal are close to 90° (Table 4), and the plane defined by Cr, P(3), C(1), C(3), and C(4) is at 92° to that defined by Cr–C(5)–Pt.

The Cr–P distance [2.35(2) Å] in (8) compares with 2.459 Å in $[\{Cr(CH_2SiMe_3)(\mu\text{-}CH_2SiMe_3)(PMe_3)\}_2]$.[11] The longer bond in the latter is probably due to the strong *trans* influence of the CH_2SiMe_3 groups whereas in (8) the semi-bridging CO ligand is *trans* to the chromium-bonded PMe_3 group. The Pt–P distances in (8) [mean 2.29(1) Å] are similar to those found previously [2.267(9)—2.331(5)];[9c] with Pt–P(1) the longer separation is due to the greater *trans* influence of the bridging $C(CO_2Me)Ph$ group.[2]

It is interesting that the salts (1) and (4), which do not contain a PMe_3 ligand bonded to chromium or tungsten, do not react with ethoxide ion to give products having bridging $C(CO_2Et)Ph$ groups. This might suggest a structural difference between the species (1) and (4), and (6), (7), (10), and (12). Evidently at some stage the ester group is generated *via* alkoxide attack on a CO group of (6), (10), or (12), and since the products contain five carbonyl groups whilst the reactants have only four the reactions are non-stoicheiometric. Presumably intermolecular CO transfer is involved in the formation of (8), (9), (11), (13), and (15), and indeed this may account for the relatively poor yields of *ca.* 35—55% for the chromium complexes, which are not improved by carrying out the reactions under a CO atmosphere. In view of the fact that CO groups attached to cationic metal centres are well known to undergo facile attack by alkoxide, and following the recent observation[15] that nucleophilic attack of the anions $[M(CO)_5]^-$ (M = Mn or Re) on $[Mn{\equiv}CC_6H_4Me\text{-}4(CO)_2(\eta\text{-}C_5H_5)]^+$ affords dimetal compounds $[MMn\{\mu\text{-}C(CO)C_6H_4Me\text{-}4\}(CO)_6(\eta\text{-}C_5H_5)]$ containing a bridging $\mu\text{-}C(CO)C_6H_4Me\text{-}4$ group, two plausible mechanisms for ester group formation in (8), (9), (11), (13), and (15) can be suggested. Thus nucleophilic attack of alkoxide ion might occur on a CO group bound to a cationic Cr or W metal centre in (6), (10), or (12), and the resulting ester group might migrate to the bridging carbon. This process might be facilitated if in the salts one of the CO ligands is leaning towards the bridging carbon atom and is interacting with it. Indeed in view of the formation of the bridging ketene species mentioned above, it is possible that alkoxide ion attack occurs on a positively charged CO already bound to the bridging carbon atom, *i.e.* our formulation for (6), (7), (10), and (12) might be incorrect and these salts are ylide-like in character, *viz.* $\mu\text{-}C(\overset{+}{C}O)R$. Further studies are in hand to elucidate the structures of the salts, although at present, as mentioned earlier, crystals suitable for an *X*-ray diffraction study have not been isolated. However, in the interim, attention has been directed towards manganese– and rhenium–platinum complexes containing bridging alkylidene and alkylidyne groups. Compounds containing the ring system $\overline{Mn\{\mu\text{-}C(OMe)Ph\}Pt}$ have been prepared,[3] but for the present study the complex (16) was synthesized by addition of $[Mn\{C(OMe)C_6H_4Me\text{-}4\}(CO)_2(\eta\text{-}C_5H_5)]$ to $[Pt(C_2H_4)(PMe_3)_2]$, generated *in situ* from $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene). Treatment of (16) with $[OMe_3][BF_4]$ afforded the dark red compound (17), which crystallises with one molecule of dichloromethane per molecule of complex. The rhenium–platinum complexes (18)—(21) were prepared from $[Re\{C(OMe)C_6H_4Me\text{-}4\}(CO)_2(\eta\text{-}C_5H_5)]$ and $[Pt(C_2H_4)(PR_3)_2]$ *via* a similar sequence of reactions. The salt (21) was also prepared by treating $[Re{\equiv}CC_6H_4Me\text{-}4(CO)_2(\eta\text{-}C_5H_5)]^+$ with $[Pt(C_2H_4)(PMe_2Ph)_2]$.



	M	L
(17)	Mn	PMe_3
(19)	Re	PMe_3
(21)	Re	PMe_2Ph

It was possible to characterise compounds (16)—(21) (Table 1) by their ^1H (see Experimental section), ^{31}P, and ^{13}C (Table 6) n.m.r. spectra.

The ^{31}P n.m.r. spectra of (16)—(21) each showed the two resonances expected for the presence of the $Pt(PR_3)_2$ groups, with $^{195}Pt\text{–}^{31}P$ couplings of similar magnitude to those observed previously.[1-3] The larger coupling (*ca.* 4 500 Hz) is assigned to the PR_3 ligand which is *trans* to the metal atom.[2,3] For each compound the ^1H n.m.r. spectrum (see Experimental section) shows signals for all the expected proton environments. The ^{13}C n.m.r. spectra are of greater interest since it was possible in each compound to detect the resonance of the bridging carbon atom. For the neutral bridged alkylidene compounds (16), (18), and (20) the shifts are at δ 193.6, 166.0, and 165.4 p.p.m. respectively, and each signal is a doublet as a result of coupling [$J(^{31}P\text{–}^{13}C)$, *ca.* 75 Hz] with presumably the PR_3 ligand *trans* to the μ-C(OMe)C_6H_4Me-4 group. The chemical shifts observed for the bridge carbene-carbon atoms in (16), (18), and (20) may be compared with that observed for this atom (198 p.p.m.) in the ^{13}C spectrum of [MnPt{μ-C(OMe)Ph}$(CO)_2$(cod)-(η-C_5H_5)].[3] These shifts are all more shielded than those observed in the spectra of the parent mononuclear metal–carbene complexes [M{C(OMe)C_6H_4Me-4}$(CO)_2$(η-C_5H_5)] (M = Mn, δ 334.8; M = Re, δ 288.1 p.p.m.).

In the ^{13}C n.m.r. spectra of the salts (17), (19), and (21) the bridging alkylidyne carbon atoms show resonances at δ 338.1, 385.2, and 382.6 p.p.m., respectively. These signals are doublets [$J(^{31}P-^{13}C)$, 71—66 Hz], and have ^{195}Pt satellites. The $^{195}Pt-^{13}C$ coupling constants of 730, 745, and 757 Hz (Table 6) are similar in magnitude to those we have reported earlier for related compounds. Thus in the ^{13}C n.m.r. spectrum of [PtW(μ-CC_6H_4Me-4)$(CO)_2(PMe_3)_2$(η-C_5H_5)], which is isoelectronic with (19), δ = 338 p.p.m. for μ-C, with $J(^{195}Pt-^{13}C) = 732$ Hz.[4] In the neutral platinum–tungsten complex the resonance is less deshielded than in the cationic species, where for (19) δ = 385.2 p.p.m. The highly deshielded nature of carbyne-carbon atoms in dimetal cations has been commented on elsewhere.[16]

TABLE 6

Phosphorus-31 and ^{13}C n.m.r. data [a] for the platinum–manganese and –rhenium complexes

	Complex	$^{31}P(\delta)$ [b]	$^{13}C(\delta)$ [c]
(16)	[MnPt{μ-C(OMe)C_6H_4Me-4}$(CO)_2(PMe_3)_2$(η-C_5H_5)]	15.7 [s, J(PPt) 2 441] 21.5 [s, J(PPt) 4 670]	235.3 [CO, J(PtC) 27], 232.4 [CO, J(PtC) 41], 193.6 [μ-C, d, J(PC) 73], 157.3 [$C^1(C_6H_4)$, J(PtC) 60], 131.6, 126.6, 119.2 [C^2—$C^6(C_6H_4)$], 88.3 (C_5H_5), 57.6 [OMe, J(PtC) 49], 20.9 (Me-4), 18.0—17.0 (MeP)
(17)	[MnPt(μ-CC_6H_4Me-4)$(CO)_2(PMe_3)_2$(η-C_5H_5)][BF_4]	41.1 [d, J(PP) 2, J(PPt) 4 043] 45.6 [d, J(PP) 2, J(PPt) 2 576]	338.1 [d, μ-C, J(PC) 71, J(PtC) 757], 227.2 [d, CO, J(PC) 12, J(PtC) 81], 160.0 [$C^1(C_6H_4)$, J(PtC) 86], 140.8, 129.4, 120.0 [C^2—$C^6(C_6H_4)$], 90.8 (C_5H_5), 21.7 (Me-4), 18.6—15.2 (MeP)
(18)	[PtRe{μ-C(OMe)C_6H_4Me-4}$(CO)_2(PMe_3)_2$(η-C_5H_5)]	17.4 [d, J(PP) 12, J(PPt) 2 463] 24.5 [d, J(PP) 12, J(PPt) 4 705]	205.4 [CO, J(PtC) 17], 203.2 [CO, J(PtC) 19], 166.0 [d, μ-C, J(PC) 78], 159.3 [$C^1(C_6H_4)$, J(PtC) 49], 131.4—126.7 [C^2—$C^6(C_6H_4)$], 86.8 (C_5H_5), 58.0 [OMe, J(PtC) 44], 20.8 (Me-4), 19—14 (MeP)
(19)	[PtRe(μ-CC_6H_4Me-4)$(CO)_2(PMe_3)_2$(η-C_5H_5)][BF_4]	8.1 [d, J(PP) 2, J(PPt) 4 336] 16.5 [d, J(PP) 2, J(PPt) 2 585]	385.2 [d, μ-C, J(PC) 67, J(PtC) 745], 200.1 (CO), 159.8 [$C^1(C_6H_4)$, J(PtC) 70], 140.0, 129.2, 120.2 [C^2—$C^6(C_6H_4)$], 90.6 (C_5H_5), 21.4 (Me-4), 18.6—14.9 (MeP)
(20)	[PtRe{μ-C(OMe)C_6H_4Me-4}$(CO)_2(PMe_2Ph)_2$(η-C_5H_5)]	7.7 [d, J(PP) 10, J(PPt) 2 486] 14.4 [d, J(PP) 10, J(PPt) 4 837]	205.2 [CO, J(PtC) 17], 203.5 [CO, J(PtC) 12], 165.4 [d, μ-C, J(PC) 77], 159.3 [$C^1(C_6H_4)$, J(PtC) 46], 140—126 [C^2—C^6-(C_6H_4), Ph], 86.9 (C_5H_5), 58.4 [OMe, J(PtC) 41], 20.9 (Me-4), 16—13 (MeP)
(21)	[PtRe(μ-CC_6H_4Me-4)$(CO)_2(PMe_2Ph)_2$(η-C_5H_5)][BF_4]	−1.5 [d, J(PP) 1, J(PPt) 4 445] 7.0 [d, J(PP) 1, J(PPt) 2 653]	382.6 [d, μ-C, J(PC) 66, J(PtC) 730], 200.0 (CO), 160.1 [$C^1(C_6H_4)$, J(PtC) 66], 140, 136—120 [C^2—$C^6(C_6H_4)$, Ph], 91.5 (C_5H_5), 21.7 (Me-4), 16—12 (MeP)

[a] ^1H-decoupled spectra, measured in $CDCl_3$. Coupling constants in Hz. [b] In p.p.m. to low frequency of 85% H_3PO_4 (external). In p.p.m. to high frequency of $SiMe_4$.

It is interesting to compare the chemical shifts shown by the bridging carbyne-carbon atoms in the dimetal species (19) and (21) with those observed for the carbyne-carbon atom in the mononuclear compound [Re≡CC_6H_4Me-4$(CO)_2$(η-C_5H_5)][BF_4] (δ = 315.3 p.p.m.). In the dimetal compounds the carbyne-carbon atoms are more deshielded, in contrast to the increase in shielding which occurs in passing from a mononuclear carbene complex to the dimetal bridged counterpart.

The compounds (17) and (21) reacted quantitatively with sodium methoxide in methanol to regenerate the neutral dimetal carbene complexes (16) and (20) respectively. There was no evidence for formation of dimetal species containing μ-C(CO_2Me)C_6H_4Me-4 ligands. Thus the manganese–platinum and –rhenium compounds differ in behaviour from the chromium and tungsten salts (6), (10), and (12), discussed above.

Crystals of (17) were of good quality, and an *X*-ray diffraction study was undertaken. The results are summarised in Tables 7—9, and the cation is shown in Figure 2 with the atomic numbering scheme.

It is seen that the manganese–platinum bond is bridged by the CC_6H_4Me-4 group, as anticipated from the ^{13}C n.m.r. spectrum. The Mn–Pt separation [2.628(1) Å] is somewhat less than that found (mean 2.675 Å) in the two forms of [MnPt(μ-C_4H_5O)$(CO)_4$-$(PMe_3)_2$],[3] but not appreciably so. Interest centres on the Mn–C separation [1.829(8) Å] which is substantially

TABLE 7

Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses for complex (17)

Atom	x	y	z
Pt	1.166 00(3)	0.402 98(2)	0.158 43(2)
Mn	0.981 4(1)	0.320 2(1)	0.202 8(1)
P(1)	1 275 5(2)	0.500 4(1)	0.202 5(2)
P(2)	1.270 9(3)	0.381 2(2)	0.027 2(2)
C(31)	0.934(1)	0.216 9(4)	0.154 1(6)
C(32)	0.860(1)	0.234 0(4)	0.227 0(6)
C(33)	0.946(1)	0.246 6(4)	0.303 8(6)
C(34)	1.073(1)	0.237 3(4)	0.278 4(6)
C(35)	1.066(1)	0.219 0(4)	0.185 8(6)
C	1.083 8(8)	0.381 0(4)	0.269 4(6)
C(41)	1.112 9(9)	0.392 7(4)	0.363 9(5)
C(42)	1.242 3(9)	0.396 0(5)	0.399 8(6)
C(43)	1.269(1)	0.410 1(5)	0.492 5(6)
C(44)	1.171(1)	0.422 4(4)	0.547 7(6)
C(45)	1.040(1)	0.418 0(5)	0.512 5(6)
C(46)	1.013 1(9)	0.402 6(5)	0.421 2(6)
C(47)	1.204(1)	0.442 3(6)	0.646 8(6)
C(11)	1.200(1)	0.552 9(5)	0.284 9(8)
C(12)	1.444(1)	0.492 3(7)	0.249 5(9)
C(13)	1.281(1)	0.562 1(6)	0.109 1(8)
C(21)	1.214(2)	0.424 1(8)	−0.079 0(8)
C(22)	1.260(1)	0.289 4(6)	−0.003 0(7)
C(23)	1.445(1)	0.396 1(8)	0.037 6(9)
C(1)	0.994(1)	0.345 4(5)	0.085 9(7)
O(1)	0.968 5(7)	0.346 6(4)	0.009 3(4)
C(2)	0.846(1)	0.377 3(6)	0.205 1(7)
O(2)	0.760 7(9)	0.414 4(5)	0.207 8(7)
C(3) *	0.580(1)	0.186 2(8)	−0.030(1)
Cl(1)	0.645 0(5)	0.104 4(2)	−0.030 0(4)
Cl(2)	0.698 9(4)	0.251 2(3)	−0.022 5(3)
B	0.464(2)	0.216 8(9)	0.238 8(9)
F(1)	0.401(2)	0.200 1(9)	0.168 5(8)
F(2)	0.435(2)	0.182(1)	0.306 6(9)
F(3)	0.462(3)	0.277 6(8)	0.253(1)
F(4)	0.569(1)	0.196(1)	0.233(1)

* Complex crystallises with one molecule of CH_2Cl_2.

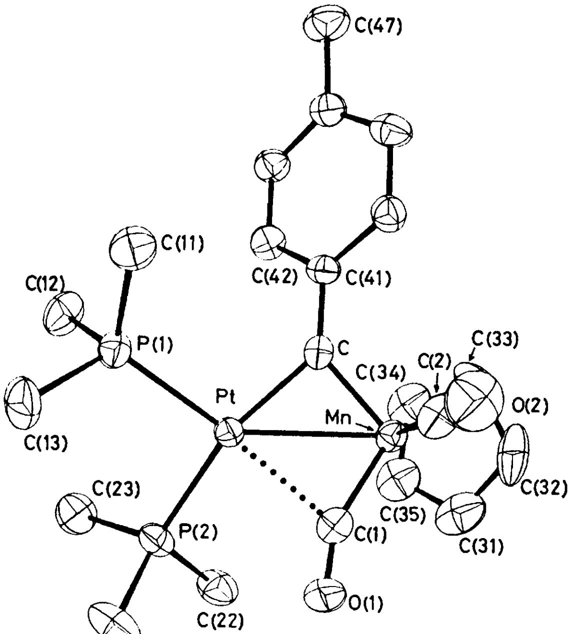


FIGURE 2 ORTEP diagram (40% probability ellipsoids) showing the molecular structure and atomic numbering scheme for the cation $[MnPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]^+$

shorter than manganese–carbon σ bonds (2.16 Å),[17] and is comparable with the Mn–C(carbene) bond (1.88 Å) in $[Mn\{C(COPh)Ph\}(CO)_2(\eta\text{-}C_5H_5)]$.[18] In the dimanganese complexes $[Mn_2(\mu\text{-}CH_2)(CO)_4(\eta\text{-}C_5H_4Me)_2]$ [19] and $[Mn_2(\mu\text{-}C{=}CHPh)(CO)_4(\eta\text{-}C_5H_5)_2]$,[20] the Mn–μ-C distances, 2.013(4) and 1.97(1) Å respectively, are longer than that in (17). These data strongly suggest that in (17) the Mn–μ-C linkage is a double bond, thus giving the manganese atom an 18-electron configuration. The Pt–μ-C distance [1.967(8) Å] is at the short end of the range (1.99—2.15 Å) generally associated with such bonds but is very close to that found [1.997(9) Å] in the neutral alkylidyne-bridged compound $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$.[4] The Mn–C–Pt angle of 87.5(4) Å

TABLE 8

Bond lengths (Å) and angles (°) for the complex $[MnPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)][BF_4]\cdot CH_2Cl_2$ (17)

(*a*) Distances

Pt–Mn	2.628(1)		
Pt–C	1.967(8)	Mn–C	1.829(8)
Pt–P(1)	2.274(2)	Pt–P(2)	2.351(3)
Mn–C(1)	1.82(1)	C(1)–O(1)	1.15(1)
Mn–C(2)	1.80(1)	C(2)–O(2)	1.15(1)
C–C(41)	1.44(1)	C(41)–C(42)	1.42(1)
C(42)–C(43)	1.41(1)	C(43)–C(44)	1.39(1)
C(44)–C(47)	1.54(1)	C(44)–C(45)	1.43(2)
C(45)–C(46)	1.40(1)	C(46)–C(41)	1.41(1)
C(31)–C(32) [a]	1.42	C(32)–C(33)	1.42
C(33)–C(34)	1.42	C(34)–C(35)	1.42
C(35)–C(31)	1.42		
Mn–C(31)	2.17(1)	Mn–C(32)	2.14(1)
Mn–C(33)	2.13(1)	Mn–C(34)	2.14(1)
Mn–C(35)	2.17(1)		
P(1)–C(11)	1.82(1)	P(1)–C(12)	1.85(1)
P(1)–C(13)	1.84(1)	P(2)–C(21)	1.84(1)
P(2)–C(22)	1.83(1)	P(2)–C(23)	1.83(1)
C(3)–Cl(1) [b]	1.72(2)	C(3)–Cl(2)	1.77(2)
B–F(1)	1.24(2)	B–F(2)	1.27(2)
B–F(3)	1.19(2)	B–F(4)	1.17(2)

(*b*) Angles

P(1)–Pt–Mn	142.5(1)	P(1)–Pt–P(2)	97.6(1)
P(1)–Pt–C	100.3(2)	P(1)–Pt–C(1)	152.9(3)
Mn–Pt–P(2)	119.8(1)	Mn–Pt–C	44.1(2)
Mn–Pt–C(1)	42.8(2)	P(2)–Pt–C	157.2(3)
P(2)–Pt–C(1)	85.4(3)	C–Pt–C(1)	85.2(3)
Pt–Mn–C	48.4(3)	Pt–Mn–C(1)	59.2(3)
C–Mn–C(1)	105.3(4)	Pt–P(1)–C(11)	115.0(4)
Pt–P(1)–C(12)	118.8(4)	Pt–P(1)–C(13)	111.3(4)
C(11)–P(1)–C(12)	104.0(6)	C(11)–P(1)–C(13)	100.9(6)
C(12)–P(1)–C(13)	104.9(6)	Pt–P(2)–C(21)	119.6(5)
Pt–P(2)–C(22)	110.7(4)	Pt–P(2)–C(23)	115.0(4)
C(21)–P(2)–C(22)	102.4(6)	C(21)–P(2)–C(23)	104.7(7)
C(22)–P(2)–C(23)	102.4(6)	Pt–C(1)–O(1)	124.5(8)
Pt–C(1)–Mn	78.0(4)	Mn–C(1)–O(1)	157.5(9)
C(2)–Mn–Pt	102.9(4)	C(2)–Mn–C(1)	88.2(5)
C(2)–Mn–C	91.2(4)	Mn–C(2)–O(2)	179(1)
Pt–C–C(41)	135.8(6)	Pt–C–Mn	87.5(4)
C(41)–C–Mn	134.8(6)	C(35)–C(31)–C(32)	108
C(31)–C(32)–C(33) [a]	108	C(32)–C(33)–C(34)	108
C(33)–C(34)–C(35)	108	C(34)–C(35)–C(36)	108
C–C(41)–C(42)	120.1(8)	C–C(41)–C(46)	120.4(8)
C(46)–C(41)–C(42)	119.4(8)	C(41)–C(42)–C(43)	119.3(9)
C(42)–C(43)–C(44)	120.8(9)	C(43)–C(44)–C(45)	120.3(8)
C(44)–C(45)–C(46)	118.9(9)	C(45)–C(46)–C(41)	121.1(9)
C(43)–C(44)–C(47)	119(1)	C(45)–C(44)–C(47)	120.5(9)
Cl(1)–C(3)–Cl(2) [b]	112(1)		
F(1)–B–F(2)	113(2)	F(1)–B–F(3)	113(2)
F(1)–B–F(4)	107(2)	F(2)–B–F(3)	112(2)
F(2)–B–F(4)	99(2)	F(3)–B–F(4)	113(2)

[a] Parameters not refined, no estimated standard deviations.
[b] Dichloromethane solvate.

in (17) may be compared with that of Cr–C(5)–Pt [77(1)°] in the alkylidene compound (8) and W–μ-C–Pt [87.9(3)°] in the alkylidyne compound [$PtW(\mu$-CC_6H_4Me-4)$(CO)_2(PMe_2Ph)_2(\eta$-$C_5H_5)$].[4] In the latter compound carbon atoms of the μ-CC_6H_4Me-4 ligand define a plane which is at 88.1° to the Pt–μ-C–W ring, whereas in (17) the bridging ligand is much more tilted (43°) to the Pt–μ-C–Mn ring (Table 9).

The *X*-ray results reveal that one of the CO ligands in (17) is semi-bridging [Mn–C(1)–O(1) 157.5(9)°]; as with (8) the degree of M–C–O bending is half-way between that for a linear M–Ċ–O group and that for a symmetrical M(μ-CO)M bridge.[13] The Pt–C(1) distance is 2.31(1) Å, compared with 2.21(3) Å found for the semi-bridging carbonyls in [$Pt_3(\mu$-$CO)_3\{P(C_6H_{11})_3\}_3$].[21] In (17), as in (8), the semi-bridging carbonyl evidently provides a mechanism whereby the electron-rich platinum atom can transfer electron density back to the $Mn(CO)_2(\eta$-$C_5H_5)$ group. The presence of a CO band in the i.r. of (17) at 1 829 cm^{-1} is thus explained, although on the n.m.r. time scale both CO ligands are equivalent (Table 6).

TABLE 9

Some least-squares planes * for the cation [$MnPt(\mu$-CC_6H_4-Me-4)$(CO)_2(PMe_3)_2(\eta$-$C_5H_5)]^+$; distances (Å) of atoms from the planes are given in square brackets

Plane (i): Mn, Pt, C

$$6.848x - 14.039y + 2.289z = 2.689$$

Plane (ii): Pt, P(1), P(2)

$$6.689x - 10.743y + 7.128z = 4.599$$

Plane (iii): C, Mn, Pt, P(1), P(2)

$$7.034x - 11.083y + 6.143z = 4.784$$

[Pt −0.08, Mn −0.18, C 0.27, P(1) −0.11, P(2) 0.10, C(1) 1.09]

Plane (iv): C, C(41) to C(47)

$$0.308x + 18.891y - 3.166z = 6.615$$

[C(41) −0.01, C(42) −0.02, C(43) −0.04, C(44) −0.01, C(45) −0.02, C(46) −0.03, C(47) 0.06, C 0.06]

Dihedral angles (°) between least-squares planes

	(ii)	(iii)	(iv)
(i)	21.1	17.4	42.8
(ii)		4.2	50.0

* *x*, *y*, and *z* are fractional crystal co-ordinates.

The platinum atom in (17) is in an essentially planar environment with respect to P(1), P(2), C, and Mn, since the dihedral angle between the planes defined by P(1)–P(2)–Pt and C–Mn–Pt is only 21°. The Pt–P distances [2.312(2) Å average] fall within the range previously observed.[22] However, Pt–P(2) is somewhat longer than Pt–P(1) perhaps reflecting the *trans* influence of the carbyne-carbon atom.[4]

EXPERIMENTAL

The instrumentation used was as described in earlier parts of this series. Light petroleum refers to that fraction of b.p. 40—60 °C. Hydrogen-1, ^{31}P, and ^{13}C (^1H-decoupled) n.m.r. spectra were measured at 100, 40.48, and 25.15 MHz respectively. All n.m.r. spectra were measured in [$^2H_1$]chloroform unless otherwise stated. All reactions were carried out under an atmosphere of nitrogen using Schlenk-tube techniques, and dry oxygen-free solvents. Infrared spectra were measured in cyclohexane solution unless otherwise stated. Methods described in the literature were used to prepare the compounds [$Pt(cod)_2$],[21] [$MPt\{\mu$-$C(OMe)Ph\}(CO)_5(PMe_3)_2$] (M = Cr or W),[2] and [$MPt\{\mu$-$C(OMe)R\}(CO)_4(PMe_3)_3$] (M = Cr or W; R = Ph or C_6H_4Me-4) [1,2] used in the syntheses. Analytical data for the new compounds are given in Table 1, and n.m.r. data in Tables 2 and 6.

Synthesis of the Compounds [$MPt(\mu$-$CR^1R^2)(CO)_5(PMe_3)_2$] (M = Cr *or* W).—(*a*). To a dichloromethane (20 cm^3) solution of [$CrPt\{\mu$-$C(OMe)Ph\}(CO)_5(PMe_3)_2$] (330 mg, 0.5 mmol) was added [OMe_3][BF_4] (74 mg, 0.5 mmol). After 1 h solvent was removed *in vacuo* and the oily residue washed with diethyl ether (3 × 10 cm^3). The residue was then suspended in diethyl ether (40 cm^3) and treated with a 1.5 molar solution in diethyl ether of Li[C_6H_4Me-4] (0.55 mmol) at 0 °C. After 1 h the solution was hydrolysed (10 cm^3 H_2O) and the ether layer separated and dried with Mg[SO_4]. The mixture was filtered and solvent removed *in vacuo*. The solid residue was dissolved in toluene and chromatographed on alumina. Elution with diethyl ether–light petroleum gave an orange band. Removal of solvent gave a solid which was recrystallised from diethyl ether–light petroleum to give orange *crystals* of [$PtCr\{\mu$-$C(Ph)C_6H_4Me$-4$\}(CO)_5(PMe_3)_2$] (2) (20 mg, 6%), $\nu_{max.}$ (CO) at 2 023w, 1 966m, 1 932vs, 1 892s, and 1 879s cm^{-1}.

(*b*). Similarly, [$CrPt\{\mu$-$C(OMe)Ph\}(CO)_5(PMe_3)_2$] (330 mg, 0.5 mmol) in dichloromethane (20 cm^3) was treated with [OMe_3][BF_4] (74 mg, 0.5 mmol). Removal of solvent, washing with diethyl ether, and addition of Na[OEt] (2.5 cm^3, 0.2 mol dm^{-3} in EtOH) at 0 °C to a diethyl ether (40 cm^3) suspension was followed after 1 h at room temperature by hydrolysis (10 cm^3 H_2O). The ether layer was dried and chromatographed. Elution with diethyl ether–light petroleum gave an orange solution which afforded orange *crystals* of [$CrPt\{\mu$-$C(OEt)Ph\}(CO)_5(PMe_3)_2$] (3) (15 mg, 4%) from diethyl ether–light petroleum; $\nu_{max.}$ (CO) at 2 024vs, 1 976m, 1 933vs, 1 890m, and 1 878m cm^{-1}.

(*c*). The compound [$PtW\{\mu$-$C(OMe)Ph\}(CO)_5(PMe_3)_2$] (386 mg, 0.5 mmol) in dichloromethane (20 cm^3) was treated with [OMe_3][BF_4] (74 mg, 0.5 mmol). After 1 h at room temperature the solvent was removed *in vacuo*, the residue washed with diethyl ether (3 × 10 cm^3), and treated with Na[OEt] (2.5 cm^3, 0.2 mol dm^{-3} in EtOH). After 1 h at room temperature the mixture was worked up as described above to give after chromatography and recrystallisation orange *crystals* of [$PtW\{C(OEt)Ph\}(CO)_5(PMe_3)_2$] (5) (45 mg, 11%); $\nu_{max.}$ (CO) at 2 044vs, 1 964m, 1 936vs, and 1 888vs cm^{-1}.

Preparation of the Salts [$MPt(\mu$-$CR)(CO)_4(PMe_3)_3$][BF_4] (M = Cr, R = Ph; M = W, R = C_6H_4Me-4).—(*a*). A solution of [$CrPt\{\mu$-$C(OMe)Ph\}(CO)_4(PMe_3)_3$] (659 mg, 1 mmol) in dichloromethane (20 cm^3) was treated with [OMe_3][BF_4] (148 mg, 1 mmol). After 1 h at room temperature the dark red-green mixture was filtered and diethyl ether (20 cm^3) added dropwise to give orange-brown *microcrystals* of [$CrPt(\mu$-$CPh)(CO)_4(PMe_3)_3$][BF_4] (6) (280 mg, 37%); $\nu_{max.}$ (CO) (Nujol) at 1 998vs, 1 912vs, 1 895vs, and 1 833vs cm^{-1}.

(*b*). Trimethyloxonium tetrafluoroborate (19 mg, 0.12 mmol) was added to [$PtW\{\mu$-$C(OMe)C_6H_4Me$-4$\}(CO)_4(PMe_3)_3$] (93 mg, 0.11 mmol) in methanol (5 cm^3) affording a dark green solution. After 5 min solvent was removed *in vacuo* and the residue treated with dichloromethane (10 cm^3). After filtration, the volume was reduced to *ca.* 3 cm^3 and the solution treated dropwise with diethyl ether, precipitating green *microcrystals* of [PtW(μ-CC$_6$H$_4$Me-4)(CO)$_4$(PMe$_3$)$_3$][BF$_4$] (7) which were washed with diethyl ether and dried *in vacuo* (30 mg, 30%), $\nu_{max.}$ (CO)(CH$_2$Cl$_2$), at 2 065s, 2 010m, 1 984vs, and 1 894m br cm^{-1}.

Preparation of the Chromium- and Tungsten–Platinum Complexes (8)—(15).—(*a*). Trimethyloxonium tetrafluoroborate (55 mg, 0.3 mmol) was added to [CrPt{μ-C(OMe)Ph}(CO)$_4$(PMe$_3$)$_3$] (212 mg, 0.3 mmol) in dichloromethane (10 cm^3). After 1 h at room temperature volatile material was removed *in vacuo* and the residue washed with diethyl ether (2 × 10 cm^3). The solid was suspended in diethyl ether (30 cm^3) and treated at 0 °C with Na[OMe] (1.5 cm^3, 0.24 mol dm^{-3} solution in methanol). After 1 h, water (10 cm^3) was added. The ether layer was dried (Mg[SO$_4$]), evaporated, and the oily residue in toluene (2 cm^3) chromatographed on alumina. Elution with diethyl ether–light petroleum gave, after recrystallisation, bright yellow *crystals* of [CrPt{μ-C(CO$_2$Me)Ph}(CO)$_4$(PMe$_3$)$_3$] (8) (121 mg, 55%); $\nu_{max.}$ at 1 992m, 1 915(sh), 1 909vs, 1 888vs (CO), and 1 626m br (CO$_2$Me) cm^{-1}.

(*b*). The compound [CrPt{μ-C(CO$_2$Et)Ph}(CO)$_4$(PMe$_3$)$_3$] (9) (83 mg, 37%) was obtained as bright yellow *crystals* using the same method as for the synthesis of (8). For complex (9) $\nu_{max.}$ at 1 989m, 1 906vs, 1 883s, 1 816w br (CO), and 1 640m (CO$_2$Et) cm^{-1}.

(*c*). The compound [CrPt{μ-C(OMe)C$_6$H$_4$Me-4}(CO)$_4$(PMe$_3$)$_3$] (225 mg, 0.3 mmol) in methanol (10 cm^3) was treated with [OMe$_3$][BF$_4$] (50 mg, 0.33 mmol). After reaction with Na[OMe] (1.5 mmol) in methanol (10 cm^3), chromatography on alumina gave bright yellow *crystals* of [CrPt{μ-C(CO$_2$Me)C$_6$H$_4$Me-4}(CO)$_4$(PMe$_3$)$_3$] (11) (78 mg, 35%); $\nu_{max.}$ at 1 992m, 1 914(sh), 1 909s, 1 886m (CO), and 1 625w br (CO$_2$Me) cm^{-1}.

(*d*). Trimethyloxonium tetrafluoroborate (37 mg, 0.25 mmol) was added to [PtW{μ-C(OMe)Ph}(CO)$_4$(PMe$_3$)$_3$] (210 mg, 0.25 mmol) in dichloromethane (10 cm^3). After 1 h at room temperature, solvent was removed *in vacuo* and the resulting oil washed with diethyl ether. To this oil, in diethyl ether (30 cm^3), was added Na[OMe] (0.3 mmol, 0.2 mol dm^{-3} in methanol). After 1 h water (10 cm^3) was added. The ether layer was dried (Mg[SO$_4$]), evaporated, and the residue dissolved in toluene (3 cm^3) and chromatographed. Elution with diethyl ether–light petroleum gave two yellow bands which were separated and afforded (*i*) yellow *crystals* of [PtW{μ-C(CO$_2$Me)Ph}(CO)$_4$(PMe$_3$)$_3$] (13) (40 mg, 19%), $\nu_{max.}$ at 2 012(sh), 2 008m, 1 914vs, 1 893m, 1 832w br (CO); and 1 627w (CO$_2$Me) cm^{-1}, and (*ii*) yellow *crystals* of [PtW{μ-C(CO$_2$Me)Ph}(CO)$_3$(PMe$_3$)$_4$] (14) (16 mg, 7%), $\nu_{max.}$ at 1 912vs, 1 822m, 1 807m (CO), and 1 627w (CO$_2$Me) cm^{-1}.

(*e*). Bright yellow crystals of [PtW{μ-C(CO$_2$Et)Ph}(CO)$_4$(PMe$_3$)$_3$] (15) (15% yield) were prepared in a similar manner to complex (13). For compound (15), $\nu_{max.}$ at 2 013(sh), 2 007m, 1 911vs, 1 891m, 1 837w br (CO), and 1 631w br (CO$_2$Et) cm^{-1}.

Synthesis of the Complexes [MPt{μ-C(OMe)C$_6$H$_4$Me-4}(CO)$_2$(PR$_3$)$_2$(η-C$_5$H$_5$)] (M = Mn, PR$_3$ = PMe$_3$; M = Re, PR$_3$ = PMe$_3$ *or* PMe$_2$Ph).—(*a*). A solution of [Pt(C$_2$H$_4$)(PMe$_3$)$_2$] (1 mmol) in light petroleum (30 cm^3) at 0 °C was prepared from [Pt(cod)$_2$] (412 mg, 1 mmol), ethylene, and PMe$_3$ (150 mg, 2 mmol).[2] Solid [Mn{C(OMe)C$_6$H$_4$Me-4}(CO)$_2$(η-C$_5$H$_5$)] (310 mg, 1 mmol) was added and the dark red solution was stirred (15 h). A pale yellow precipitate formed which was removed, washed with light petroleum (2 × 5 cm^3), and dried *in vacuo* affording yellow *crystals* of [MnPt{μ-C(OMe)C$_6$H$_4$Me-4}(CO)$_2$(PMe$_3$)$_2$(η-C$_5$H$_5$)] (16) (0.53 g, 80%); $\nu_{max.}$ (CO) at 1 869s and 1 813s cm^{-1}, ^{1}H n.m.r.: τ 2.7—3.1 (m, 4 H, C$_6$H$_4$), 5.78 (s, 5 H, C$_5$H$_5$), 6.78 (s, 3 H, OMe), 7.70 (s, 3 H, CH$_3$C$_6$), 8.40 [d, 9 H, MeP, *J*(PH) 8, *J*(PtH) 20], and 8.72 [d, 9 H, MeP, *J*(PH) 8, *J*(PtH) 35 Hz].

(*b*). A similar method was used to prepare yellow *crystals* of the compound [PtRe{μ-C(OMe)C$_6$H$_4$Me-4}(CO)$_2$(PMe$_3$)$_2$(η-C$_5$H$_5$)] (18) (275 mg, 58%) from [Pt(C$_2$H$_4$)(PMe$_3$)$_2$] (0.6 mmol) and [Re{C(OMe)C$_6$H$_4$Me-4}(CO)$_2$(η-C$_5$H$_5$)] (264 mg, 0.6 mmol) in light petroleum (40 cm^3), stirred for 2 h at room temperature. Compound (18) had $\nu_{max.}$ (CO) at 1 885s and 1 827s cm^{-1}; ^{1}H n.m.r.: τ 2.63—3.05 (m, 4 H, C$_6$H$_4$), 5.17 (s, 5 H, C$_5$H$_5$), 6.76 (s, 3 H, OMe), 7.71 (s, 3 H, CH$_3$C$_6$), 8.42 [d, 9 H, MeP, *J*(PH) 8, *J*(PtH) 20], and 8.75 [d, 9 H, MeP, *J*(PH) 10, *J*(PtH) 45 Hz].

(*c*). The compound [PtRe{μ-C(OMe)C$_6$H$_4$Me-4}(CO)$_2$(PMe$_2$Ph)$_2$(η-C$_5$H$_5$)] (20) (0.48 g, 65%) was obtained as yellow *crystals* from [Pt(C$_2$H$_4$)(PMe$_2$Ph)$_2$] (0.8 mmol) and [Re{C(OMe)C$_6$H$_4$Me-4}(CO)$_2$(η-C$_5$H$_5$)] (352 mg, 0.8 mmol) in light petroleum (40 cm^3). Complex (20) has $\nu_{max.}$ (CO) at 1 882s and 1 827s cm^{-1}; ^{1}H n.m.r.: τ 2.50—3.10 (m, 14 H, Ph and C$_6$H$_4$), 5.15 (s, 5 H, C$_5$H$_5$), 6.60 (s, 3 H, OMe), 7.71 (s, 3 H, CH$_3$C$_6$), 8.45 [d, 6 H, MeP, *J*(PH) 8, *J*(PtH) 20], 8.62 [d, 6 H, MeP, *J*(PH) 8, *J*(PtH) 20], 8.92 [d, 6 H, MeP, *J*(PH) 10, *J*(PtH) 40], and 9.07 [d, 9 H, MeP, *J*(PH) 10, *J*(PtH) 45 Hz].

Preparation of the Salts [MPt(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PR$_3$)$_2$(η-C$_5$H$_5$)][BF$_4$] (M = Mn, PR$_3$ = PMe$_3$; M = Re, PR$_3$ = PMe$_3$ *or* PMe$_2$Ph).—(*a*). A slurry of compound (16) (0.3 g, 0.46 mmol) in acetonitrile (15 cm^3) was treated with excess of [OMe$_3$][BF$_4$] (0.2 g, 1.4 mmol). The pale yellow solid rapidly dissolved giving a dark red solution which was stirred (15 min) and then solvent was removed *in vacuo*. The oily residue was extracted with dichloromethane and filtered through Celite. The volume was reduced to *ca.* 1 cm^3 giving, on slow addition of diethyl ether, dark red *prisms* of [MnPt(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PMe$_3$)$_2$(η-C$_5$H$_5$)][BF$_4$]·CH$_2$Cl$_2$ (17) (310 mg, 90%); $\nu_{max.}$ (CO) (in CH$_2$Cl$_2$) at 1 993s and 1 829s cm^{-1}. ^{1}H n.m.r.: τ 2.64 (m, 4 H, C$_6$H$_4$), 5.04 (s, 5 H, C$_5$H$_5$), 7.60 (s, 3 H, CH$_3$C$_6$), 8.24 [d, 9 H, MeP, *J*(PH) 8, *J*(PtH) 20], and 8.48 [d, 9 H, MeP, *J*(PH) 10, *J*(PtH) 42].

(*b*). To a solution of (18) (197 mg, 0.25 mmol) in dichloromethane (25 cm^3) was added [OMe$_3$][BF$_4$] (37 mg, 0.25 mmol). The mixture was stirred (2 h) at room temperature becoming dark red. After filtration the volume was reduced to *ca.* 3 cm^3, and diethyl ether (30 cm^3) added giving a red precipitate which was recovered, washed with diethyl ether (2 × 5 cm^3), affording red *microcrystals* of [PtRe(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PMe$_3$)$_2$(η-C$_5$H$_5$)][BF$_4$] (19) (165 mg, 78%); $\nu_{max.}$ (CO) (in CH$_2$Cl$_2$) at 1 992s and 1 865m br cm^{-1}. ^{1}H n.m.r.: τ 2.70 (m, 4 H, C$_6$H$_4$), 4.41 (s, 5 H, C$_5$H$_5$), 7.64 (s, 3 H, CH$_3$C$_6$), 8.27 [d, 9 H, MeP, *J*(PH) 9, *J*(PtH) 21], and 8.49 [d, 9 H, MeP, *J*(PH) 11, *J*(PtH) 45 Hz].

(*c*). The salt [PtRe(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PMe$_2$Ph)$_2$(η-C$_5$H$_5$)][BF$_4$] (21) (217 mg, 90%) was prepared as red *microcrystals* by the same method as for (19), using compound (20) (230 mg, 0.25 mmol) and [OMe$_3$][BF$_4$] (37 mg, 0.25 mmol). Compound (21) has $\nu_{max.}$ (CO) (in CH$_2$Cl$_2$) at 1 990s and 1 866m br cm^{-1}; ^{1}H n.m.r.: τ 2.44—2.82 (m, 14 H, C$_6$H$_4$ and Ph), 4.48 (s, 5 H, C$_5$H$_5$), 7.68 (s, 3 H, CH$_3$C$_6$), 8.30 [d, 6 H, MeP, *J*(PH) 8, *J*(PtH) 21], and 8.60 [d, 6 H, MeP, *J*(PH) 11, *J*(PtH) 45 Hz].

Compound (21) was also prepared (70% yield) by treating $[Re\equiv CC_6H_4Me\text{-}4(CO)_2(\eta\text{-}C_5H_5)][BF_4]$ (298 mg, 0.6 mmol) with $[Pt(C_2H_4)(PMe_2Ph)_2]$ (0.6 mmol) in dichloromethane (20 cm^3).

Reaction of $[MnPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)][BF_4]$ *with Sodium Methoxide*.—A deep red solution of (17) (100 mg, 0.12 mmol) in methanol (10 cm^3) was treated with excess of Na[OMe] (300 mg). The solution immediately lost its red colour and a yellow precipitate formed. Solvent was removed *in vacuo*, and the residue extracted with dichloromethane (2 × 5 cm^3). After concentration to *ca.* 1 cm^3, complex (16) (75 mg) was obtained quantitatively by slow addition of light petroleum, and identified spectroscopically.

Crystal-structure Determinations.—*Compound* (8). Crystals grow as very thin small platelets; that for data collection was of dimensions 0.02 × 0.35 × 0.1 mm, and diffracted intensities were recorded at room temperature for $2.9 \leqslant 2\theta \leqslant 55°$ on a Syntex $P2_1$ four-circle diffractometer.[23] Of the total 4 879 recorded intensities, only 2 292 had $|F| \geqslant 6\sigma(F)$, where $\sigma(F)$ is the standard deviation based on counting statistics, and these were used in the final refinement of the structure. Corrections were applied for Lorentz and polarisation effects and for the effects of *X*-ray absorption. Computations were carried out with the 'SHELX' system of programs.[24]

Crystal data. $C_{22}H_{35}CrO_6P_3Pt$, $M = 735.5$, Monoclinic, $a = 18.27(3)$, $b = 9.84(1)$, $c = 31.93(5)$ Å, $\beta = 106.2(1)°$, $U = 5\,510(12)$ Å^3, $D_m = 1.79$ (flotation), $Z = 8$, $D_c = 1.77$ g cm^{-3}, $F(000)$ 2 896, Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 54.3$ cm^{-1}, space group $A2/a$.

Compound (17). The crystal studied was a parallepiped of dimensions 0.2 × 0.2 × 0.28 mm. Diffracted intensities were measured [23] at room temperature for $2.9 \leqslant 2\theta \leqslant 55°$. Of the total 6 432 recorded intensities, 4 223 had $|F| \geqslant 5\sigma(F)$ and only these were used in the solution and refinement of the structure. Corrections were applied for Lorentz, polarisation, and *X*-ray absorption effects. Computations were made with the 'SHELX' system of programs.[24]

Crystal data. $C_{21}H_{30}BF_4MnO_2P_2Pt\cdot CH_2Cl_2$, M 798.2, Monoclinic, $a = 10.434(4)$, $b = 19.334(7)$, $c = 14.901(7)$ Å, $\beta = 94.42(4)°$, $U = 2\,997(2)$ Å^3, $D_m = 1.76$ (flotation), $Z = 4$, $D_c = 1.77$ g cm^{-3}, $F(000) = 1\,552$, Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 51.8$ cm^{-1}, space group $P2_1/c$.

Structure solutions and refinement. The data were treated by similar methods, that for (17) is given in braces. The structures were solved by the heavy-atom method and all atoms (except H) were located by successive electron-density difference syntheses. For (8) the hydrogen atoms were included at positions calculated for rigid group atoms and only common temperature factors for chemically equivalent hydrogen atoms were refined. For (17) the hydrogen atoms were not included in the computations, and as is often observed the temperature factors for the CH_2Cl_2 of solvation and in particular the BF_4^- counter ion were all high, reflecting considerable thermal motion in the crystal. Refinement converged at R 0.12 (R' 0.12) {R 0.044 (R' 0.046)}, with a mean shift-to-error ratio in the final cycle of 0.05 {0.04}. Weighting schemes were of the form $w^{-1} = 1.73[\sigma^2(F) + 0.004|F_o|^2)]$ {$w^{-1} = 1.361[\sigma^2(F) + 0.001\,|F_o|^2]$}, where $\sigma(F)$ is the estimated error in the observed structure factor based on counting statistics only. This gave a satisfactory weighting analysis for (17) whereas that for (8) was the best fit. The apparently high residual for (8) reflects the poor quality data of which less than 50% were of any significant intensity. The final electron-density difference synthesis showed many ripples in the region of 2—4 e Å^{-3} for (8) whereas there were no peaks >0.4 e Å^{-3} for (17). Scattering factors were from ref. 25 for C, O, and P, ref. 26 for hydrogen, and ref. 27 for Pt, Mn, and Cr, including corrections for the effects of anomalous dispersion. Atomic positional parameters are in Tables 3 and 7, interatomic distances and angles in Tables 4 and 8, and some least-squares planes in Tables 5 and 9. Observed and calculated structure factors, all thermal parameters, and positional parameters for the hydrogen atoms in (8) are listed in Supplementary Publication No. SUP 22953 (35 pp).*

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