Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 10.[1] Synthesis of Dicobalt– and Dirhodium–Tungsten Complexes with μ_3-Tolylidyne Groups; Crystal Structures of $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$ † and $[Rh_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(acac)_2(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)]$ ‡ (acac = Acetylacetonate)

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The compound $[W{\equiv}CC_6H_4Me\text{-}4(CO)_2(\eta\text{-}C_5H_5)]$ reacts with $[Co_2(CO)_8]$ in pentane at room temperature to give the dicobalt-tungsten complex $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$, the structure of which was established by a single-crystal *X*-ray diffraction study. The crystals are orthorhombic, space group *Pcmn* (non-standard setting of *Pnma*, no. 62), $Z = 4$, in a unit cell with lattice parameters $a = 10.067(13)$, $b = 11.806(26)$ and $c = 18.203(10)$ Å. The structure has been refined to R 0.025 (R' 0.027) for 1 565 reflections to $2\theta \leqslant 40°$ [(Mo-K_α) *X*-radiation] collected at 200 K. The molecule consists of a Co_2W isosceles triangle of metal atoms [Co–W 2.672(1) and Co–Co 2.488(1) Å] capped by a triply-bridging tolylidyne ligand [W–C 2.103(7) and Co–C 1.953(6) Å]. The carbonyl ligands are all terminal, with two on each cobalt atom approximately equatorial with respect to the metal atom plane, while the third is axial. From reactions of the compounds $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_4R)]$ (R = H or $SiMe_3$) with PMe_2Ph, $P(OMe)_3$, dppm $(Ph_2PCH_2PPh_2)$, and diars $[C_6H_4(AsMe_2)_2\text{-}1,2]$, the complexes $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_7(PMe_2Ph)(\eta\text{-}C_5H_4R)]$ (R = H or $SiMe_3$) and $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6L_2(\eta\text{-}C_5H_4R)]$ [L = PMe_2Ph, R = H or $SiMe_3$; L = $P(OMe)_3$, R = H; L_2 = dppm, R = H or $SiMe_3$; L_2 = diars, R = H] were isolated, and characterised by i.r. and n.m.r. spectroscopy. Reaction of $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$ with $Me_3SiC_2SiMe_3$ affords the cluster complex $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}Me_3SiC_2SiMe_3)(CO)_6(\eta\text{-}C_5H_5)]$. In light petroleum, at room temperature, $[Rh(acac)(CO)_2]$ (acac = acetylacetonate) and $[W{\equiv}CC_6H_4Me\text{-}4(CO)_2(\eta\text{-}C_5H_5)]$ react to give $[RhW(\mu\text{-}CC_6H_4Me\text{-}4)(acac)(CO)_3(\eta\text{-}C_5H_5)]$, and the latter with $[Rh(acac)(C_2H_4)_2]$ affords the dirhodiumtungsten compound $[Rh_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(acac)_2(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)]$. The molecular structure of this species was established by *X*-ray diffraction. Crystals, grown with $\frac{1}{2}C_6D_6$ of crystallisation, are triclinic, space group $P\bar{1}$, $Z = 2$, in a unit cell with lattice dimensions $a = 10.756(8)$, $b = 10.805(6)$, $c = 13.215(13)$ Å, $\alpha = 81.32(7)$, $\beta = 80.44(7)$, and $\gamma = 78.60(6)°$. The structure has been refined to $R = 0.057$ (R' 0.061) for 5 897 reflections to $2\theta \leqslant 60°$ collected at 293 K. The molecule has a triangular array of metal atoms [Rh–W 2.809(2) and 2.764(2), Rh–Rh 2.613(2) Å] with an essentially symmetrically triply-bridging tolylidyne ligand [μ_3-C–Rh 2.030(8) and 1.994(9), μ_3-C–W 1.991(8) Å]. There is a symmetrically bridging CO ligand associated with the Rh–Rh bond, and the two CO groups on the tungsten mildly semi-bridge the two Rh–W bonds (W–C–O 171°). The acac ligands function as bidentate oxygen donors to the rhodium atoms. Although the C_5H_5 ligand has an η^5 attachment to the tungsten atom it does not conform well with the pseudo-mirror symmetry of the molecule, and the distortion probably relates to the two different Rh–W bond lengths.

THE compounds $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PR_3)_2(\eta\text{-}C_5H_5)]$, prepared by displacing ethylene from the complexes $[Pt(C_2H_4)(PR_3)_2]$ with $[W{\equiv}CC_6H_4Me\text{-}4(CO)_2(\eta\text{-}C_5H_5)]$, contain 'dimetallacyclopropene' rings. From *X*-ray diffraction data on $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$, the μ-C–W separation was found to correspond closely to that expected for a C=W bond.[2] Rather surprisingly these platinum–tungsten compounds do not add a second $Pt(PR_3)_2$ fragment to give species containing a $Pt(\mu\text{-}RC{\equiv}WL)Pt$ unit [L = $(CO)_2(\eta\text{-}C_5H_5)$]. Because of the isolobal relationship[3] between CR and $W(CO)_2(\eta\text{-}C_5H_5)$, complexes containing the $Pt(\mu\text{-}RC{\equiv}WL)$-Pt group would be formally related to the alkyne-bridged diplatinum compounds $[(R_3P)_2Pt(\mu\text{-}RC{\equiv}CR)Pt(PR_3)_2]$; the latter are readily synthesised by addition of $Pt(PR_3)_2$ groups to the metallacyclopropene rings of the alkyne adducts $[Pt(RC_2R)(PR_3)_2]$.[4]

Although trimetal complexes $[Pt_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(PR_3)_4(\eta\text{-}C_5H_5)]$ have not as yet been isolated, iron-carbonyl fragments readily add to the compounds $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PR_3)_2(\eta\text{-}C_5H_5)]$ to give hetero-nuclear trimetal clusters $[FePtW(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_n(PR_3)_2(\eta\text{-}C_5H_5)]$ (n = 5 or 6).[5] Moreover, dicobalt octacarbonyl reacts with $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$ at room temperature in diethyl ether to give at least three products,[6] one of which was shown[7] by a single-crystal *X*-ray diffraction study (see later) to be $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$. This result prompted a direct synthesis of the latter species from $[Co_2(CO)_8]$ and $[W{\equiv}CC_6H_4Me\text{-}4(CO)_2(\eta\text{-}C_5H_5)]$. We have also investigated reactions of the tungsten carbyne complex with the rhodium compounds $[Rh(acac)L_2]$ (L = C_2H_4 or CO, acac = acetylacetonate), and the results of this work are also reported in this paper.

RESULTS AND DISCUSSION

The carbyne–tungsten complex $[W{\equiv}CC_6H_4Me\text{-}4(CO)_2(\eta\text{-}C_5H_5)]$[8] reacts readily with $[Co_2(CO)_8]$ in pentane at room temperature with evolution of CO and formation of the compound $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$ (1) in essentially quantitative yield; analytical and spectroscopic data are given in Tables 1—3. This dicobalt-

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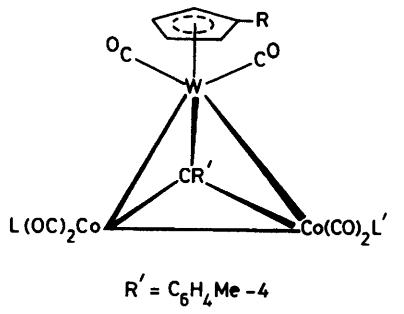
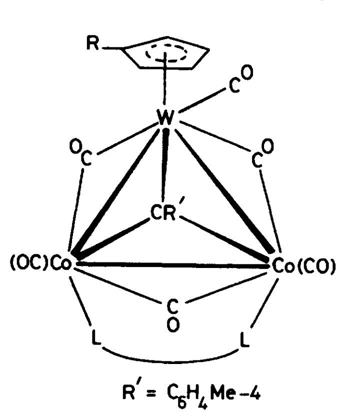
† 1,1,1,2,2,2,3,3-Octacarbonyl-3-η-cyclopentadienyl-μ_3-4-tolylidyne-*triangulo*-dicobalt-tungsten(*Co–Co*)(2*Co–W*).

‡ 1,2-Bis(acetylacetonato)-1,2-μ-carbonyl-3,3-dicarbonyl-3-η-cyclopentadienyl-μ_3-4-tolylidyne-*triangulo*-dirhodiumtungsten-*Rh–Rh*)(2*Rh–W*).



	R	L	L'
(1)	H	CO	CO
(2)	H	PMe_2Ph	CO
(3)	H	PMe_2Ph	PMe_2Ph
(4)	H	$P(OMe)_3$	$P(OMe)_3$
(7)	$SiMe_3$	PMe_2Ph	CO
(8)	$SiMe_3$	PMe_2Ph	PMe_2Ph



	R	L——L
(5)	H	$Ph_2PCH_2PPh_2$
(6)	H	$C_6H_4(AsMe_2)_2$-1,2
(9)	$SiMe_3$	$Ph_2PCH_2PPh_2$

tungsten complex has previously been prepared[9] by a very indirect route involving reaction of $[Co_3(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_9]$ with $[WAsMe_2(CO)_3(\eta\text{-}C_5H_5)]$ to give the species $[Co_3(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\mu\text{-}AsMe_2)W(CO)_3(\eta\text{-}C_5H_5)]$, which on heating in cyclohexane affords (1) and $[\{CoAsMe_2(CO)_3\}_n]$. The new synthesis described herein is more direct and proceeds in higher yield. Moreover, it provides an excellent example of the concept[3] of isolobal relationships in organometallic chemistry, because it has long been known that the reaction of alkynes with $[Co_2(CO)_8]$ yields the complexes $[Co_2(\mu\text{-}RC_2R)(CO)_6]$[10,11] having tetrahedrane-like Co_2C_2 core structures. Replacement of a CR group in the latter by $W(CO)_2(\eta\text{-}C_5H_5)$ formally produces compound (1). The presence of the capping μ_3-C atom in (1) is clearly indicated by the appearance in the ^{13}C n.m.r. spectrum (Table 3) of a signal at δ 257 p.p.m. In the well known homonuclear trimetal clusters $[Co_3(\mu_3\text{-}CR)(CO)_9]$ the alkylidyne carbon resonances occur in the range δ 250—310 p.p.m.[12] The ^{13}C n.m.r. spectrum of (1) also revealed that even at −80 °C the CO ligands are undergoing site exchange on the n.m.r. time-scale, since only one resonance is observed for these groups. As discussed below, similar behaviour occurs with several derivatives of (1). It was also observed that (1) showed (Table 2) many bands in the CO region of the i.r. spectrum, suggesting the presence of tautomers, possibly involving different rotational conformations.[13] In order to establish the structure of this dynamic molecule in the solid state a single-crystal *X*-ray diffraction study was carried out.

TABLE 1

Analytical[a] and physical data for the tungsten–cobalt and -rhodium compounds

				Analysis (%)	
Compound	M.p. (θ_c/°C)[b]	Colour	Yield (%)	C	H
(1) $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$	176—178	Dark green	95	36.4 (36.3)	1.7 (1.7)
(2) $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_7(PMe_2Ph)(\eta\text{-}C_5H_5)]$[c]	127—130	Dark green	44	41.9 (41.8)	3.1 (2.9)
(3) $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$[d]	164—170	Brown	56	45.8 (45.8)	3.9 (3.7)
(4) $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$	110	Black	70	33.2 (33.9)	3.5 (3.4)
(5) $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(dppm)(\eta\text{-}C_5H_5)]$	215—220	Dark green	60	50.8 (51.7)	3.5 (3.4)
(6) $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(diars)(\eta\text{-}C_5H_5)]$	240	Black	73	37.5 (37.7)	3.1 (3.0)
(7) $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_7(PMe_2Ph)(\eta\text{-}C_5H_4SiMe_3)]$[e]	124—126	Green	27	42.6 (42.4)	3.8 (3.8)
(8) $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(PMe_2Ph)_2(\eta\text{-}C_5H_4SiMe_3)]$	147—149	Brown	37	45.8 (46.3)	4.3 (4.3)
(9) $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(dppm)(\eta\text{-}C_5H_4SiMe_3)]$	200	Black	36	52.3 (51.6)	4.2 (3.8)
(10) $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}Me_3SiC_2SiMe_3)(CO)_6(\eta\text{-}C_5H_5)]$	202—204	Dark green	62	40.4 (40.1)	3.8 (3.7)
(11) $[RhW(\mu\text{-}CC_6H_4Me\text{-}4)(acac)(CO)_3(\eta\text{-}C_5H_5)]$	130	Dark purple	71	39.3 (39.5)	3.0 (3.0)
(12) $[Rh_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(acac)_2(CO)_3(\eta\text{-}C_5H_5)]$	160—165	Black	68	36.3 (37.2)	3.2 (3.1)

[a] Calculated values are given in parentheses. [b] With decomposition. [c] Parent ion in mass spectrum at *m/e* 804. [d] Parent ion in mass spectrum at *m/e* 914. [e] Parent ion in mass spectrum at *m/e* 876.

The results of the *X*-ray work are summarised in Tables 4 and 5, and the molecular structure is shown in Figure 1. In the crystal, the molecule is required to possess mirror symmetry; the crystallographic numbering scheme makes use of primes to indicate atoms related to one another by the mirror plane. The molecule comprises a Co_2W isosceles triangle of metal atoms [Co–W 2.672(1), Co–Co 2.488(1) Å] capped by a triply-bridging tolylidyne ligand [W–C 2.103(7), Co–C 1.953(6) Å]. The molecular mirror plane is defined (Figure 1) by the atoms W, C(1), C(2), C(5), and C(51) of the tolylidyne ligand, C(01) of the cyclopentadienyl ligand, and by the midpoints of all symmetry-related pairs. The plane of the tolylidyne ligand lies perpendicular to the mirror plane. The carbonyl ligands are all terminal, with M–C–O angles ranging from 177.0(5) to 179.7(3)° and, as often occurs with this geometry, two of the CO ligands on each Co atom are approximately equatorial with respect to the metal atom plane, while the third is axial. The two carbonyl ligands on the tungsten atom are at an interaxial angle of 82°. The structural dimensions of the molecule are extremely close to those found[9] in $[Co_2Mo(\mu_3\text{-}CPh)(CO)_8(\eta\text{-}C_5H_5)]$ despite the substitution of Mo for W and of Ph for C_6H_4Me-4; the configuration is also immediately comparable with that of the $[Co_3(\mu_3\text{-}CR)(CO)_9]$ series of clusters, from which the title compound may be considered to be derived by substitution of a $W(CO)_2(\eta\text{-}C_5H_5)$ group for a $Co(CO)_3$ moiety. The Co–Co bond length in $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$ is slightly shorter than that found in $[Co_2(CO)_8]$ [2.522(2) Å][14] but extremely close to the values found for non-CO-bridged Co–Co vectors in the species $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5Me_5)_2]$,[15] $[Co_3(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_3(\eta\text{-}C_5H_5)_2]$,[16] and $[Co_3(\mu_3\text{-}CPh)(CO)_6(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)]$.[17] Comparative values for the length of the Co–W bonds are few; in the complex $[W(\eta\text{-}C_5H_5)\{C(CF_3){=}C(CF_3)C(CF_3){=}C(CF_3)\}(CO)_2Co(CO)_2]$[18] a length of 2.664(1) Å was found, and in $[(\eta\text{-}C_5Me_5)Co(\mu\text{-}CO)\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Me){=}CHMe\}W(CO)(\eta\text{-}C_5H_5)][BF_4]$ the bond length is 2.552(1) Å,[19] but the relative shortness of this bond may be a consequence of enhanced bond order. Other features of the molecular configuration of (1) call for no special comment.

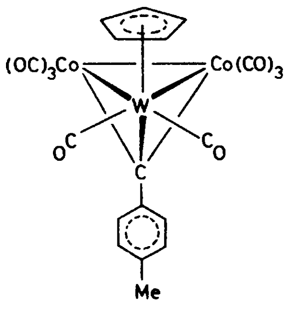
TABLE 2

Infrared [a] and phosphorus-31 n.m.r. [b] data for the complexes

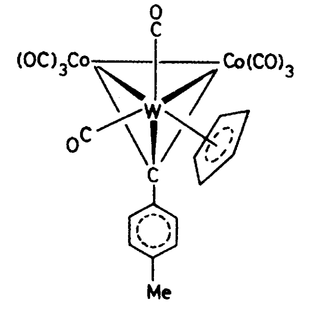
Compound	$\tilde{\nu}(CO)/cm^{-1}$	δ/p.p.m. [c] (temp./°C)
(1)	2 099m, 2 067m, 2 038s, 2 029s, 2 016m, 2 003s, 1 995w, 1 941w, 1 917w, 1 873w	
(2)	2 055w, 2 041m, 2 001s, 1 995s, 1 983s, 1 967s, 1 923m, 1 869w, 1 825w br	6.9 (−56)
(3)	2 041s, 2 017s, 2 001s, 1 997s, 1 981s, 1 961s, 1 925s, 1 881m, 1 853m, 1 815m br	3.4 (−80)
(4) [d,e]	2 031s, 2 011m, 1 987m, 1 983s, 1 971m, 1 951s, 1 927m, 1 901m, 1 851w	153.4 (25)
(5) [f]	2 013s, 2 001m, 1 981s, 1 973w, 1 965s, 1 961s, 1 889m br, 1 825w	27.3 (−50)
(6) [d]	2 019s, 1 975s, 1 951s, 1 927s, 1 887s, 1 795s	
(7)	2 059m, 2 042s, 2 003s, 1 994s, 1 967s, 1 936s, 1 921m, 1 872w, 1 820w	6.1 (−60)
(8)	2 047w, 2 023m, 2 007m, 1 999w, 1 987s, 1 967m, 1 947w, 1 885m, 1 851w, 1 807w	−2.0 (−20)
(9)	2 019s, 1 990s, 1 964s, 1 947m, 1 881s, 1 830w	29.4 (−60)
(10)	2 077w, 2 057w, 2 047m, 2 027s, 2 009s, 1 997w, 1 961w, 1 881s	
(11)	2 009m, 1 959s, 1 881m	
(12)	1 912s, 1 865m, 1 825m	

[a] Measured in methylcyclohexane unless otherwise stated. [b] Measured in $[^2H_2]$dichloromethane–dichloromethane mixture, unless otherwise stated, and at the temperatures indicated (see text). [c] Hydrogen-1 decoupled, chemical shifts in p.p.m. to high frequency of 85% H_3PO_4 (external). [d] Infrared spectrum measured in cyclohexane. [e] Phosphorus-31 n.m.r. spectrum measured in $CDCl_3$. [f] Infrared spectrum measured in dichloromethane.

The *X*-ray diffraction results for (1) establish that it adopts the conformation (1a) in the crystal, so that the appearance in the i.r. spectrum (methylcyclohexane) of ten CO stretching bands (Table 2) must indicate the presence of isomers. An equilibrium between the rotational isomers (1a) and (1b) could give rise to additional bands, but the possibility of an isomer in solution with semi-bridging CO ligands must also be considered in view of the band at 1 873 cm^{-1}. The compounds $[Co_3(\mu_3\text{-}CR)(CO)_9]$ generally show only four i.r.-active CO stretching bands but a fifth low-intensity peak is sometimes observed.[20]



(1a)



(1b)

Substitution reactions of (1) with the Lewis bases PMe_2Ph, $P(OMe)_3$, $Ph_2PCH_2PPh_2$ (dppm), and $C_6H_4(AsMe_2)_2$-1,2 (diars) afford complexes (2)—(6), data for which are summarised in Tables 1—3. The compounds (7)—(9) were prepared in a similar manner from $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_4SiMe_3)]$.[5] Rigorously dried solvents must be used in synthesis and purification of the $\eta\text{-}C_5H_4SiMe_3$ derivatives since traces of moisture lead to partial conversion to the corresponding $\eta\text{-}C_5H_5$ species, a process readily detected by ^1H n.m.r. studies.

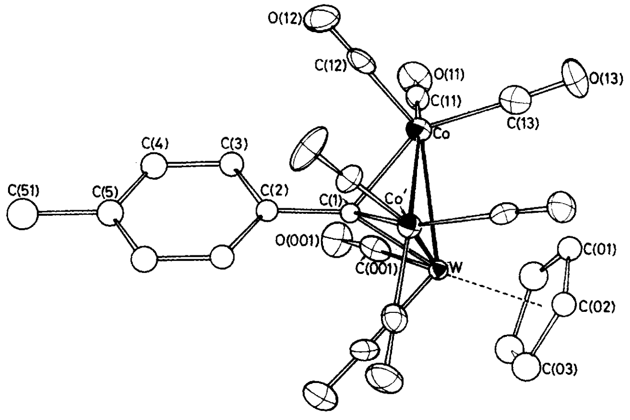


FIGURE 1 Molecular structure of $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$ (1) showing the atom numbering scheme

With the possible exception of (9), it is evident from the i.r. spectra (Table 2) that all the compounds exist in solution as mixtures of isomers since for each complex too many CO stretching bands are observed to correspond to a single molecular structure. Moreover, the occur-

TABLE 3

Hydrogen-1 and carbon-13 n.m.r. data [a]

Compound	^1H (δ/p.p.m.)	^{13}C (δ/p.p.m.) [b]
(1) [c, d, e]	2.11 (s, 3 H, $C_6H_4\mathit{Me}$), 4.52 (s, 5 H, C_5H_5), 6.98, 7.41 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8.5]	257 (μ-*C*C_6H_4Me-4), 202 (CO), 159 (C^1, C_6H_5Me-4), 136—128 (C_6H_4), 90 (C_5H_5), 21 (Me)
(2) [f]	1.44 [d, 3 H, MeP, *J*(PH) 8], 1.52 [d, 3 H, MeP, *J*(PH) 8], 2.3 (s, 3 H, $C_6H_4\mathit{Me}$), 5.1 (s, 5 H, C_5H_5), 6.9—7.3 (m, 9 H, C_6H_4 and Ph)	267 (μ-*C*C_6H_4Me-4), 208 (CO), 161 (C^1, C_6H_4Me-4), 140—126 (C_6H_4, Ph), 91 (C_5H_5), 20 ($C_6H_4\mathit{Me}$), 17.5 [d, MeP, *J*(PC) 25], 16.3 [d, MeP, *J*(PC) 25]
(3) [f]	1.62 (m, br, 12 H, MeP), 2.3 (s, 3 H, $C_6H_4\mathit{Me}$), 4.9 (s, 5 H, C_5H_5), 6.8—7.6 (m, 14 H, C_6H_4 and Ph)	264 (μ-*C*C_6H_4Me-4), 215 (CO), 164 (C^1, C_6H_4Me-4), 142—128 (C_6H_4, Ph), 93 (C_5H_5), 21 (Me-4), 18.4 [d, MeP, *J*(PC) 20], 17.6 [d, MeP, *J*(PC) 20]
(4) [g, h]	2.3 (s, 3 H, $C_6H_4\mathit{Me}$), 3.56 (s, br, 18 H, OMe), 5.1 (s, 5 H, C_5H_5), 7.15 (m, 4 H, C_6H_4)	211 (CO), 163 (C^1, C_6H_4Me-4), 133, 129, 127 (C_6H_4), 92 (C_5H_5), 52 (OMe), 21 (Me-4)
(5) [g, i]	2.35 (s, 3 H, $C_6H_4\mathit{Me}$), 3.14 [t, 2 H, CH_2, δ $H_a \approx H_b$, *J*(PH) average 10], 5.2 (s, 5 H, C_5H_5), 6.5 (m, 4 H, C_6H_4), 7.1 (m, 20 H, Ph)	265 (μ-*C*C_6H_4Me-4), 220 (WCO), 211, 204 (CoCO), 162 (C^1, C_6H_4Me-4), 138—127 (C_6H_4, Ph), 91 (C_5H_5), 28 [t, CH_2, *J*(PC) 22], 21 (Me-4)
(6) [e, i]	1.4 (m, 12 H, MeAs), 2.24 (s, 3 H, $C_6H_4\mathit{Me}$), 4.82 (s, 5 H, C_5H_5), 6.8—7.4 (m, 8 H, C_6H_4)	264 [μ-*C*C_6H_4Me-4, *J*(WC) 159], 203 (CO), 165 (C^1, C_6H_4Me-4), 143—127 (C_6H_4), 93 (C_5H_5), 21 (Me-4), 15, 13 (MeAs)
(7) [f, j]	0.24 (s, 9 H, $SiMe_3$), 1.42 [d, 3 H, MeP, *J*(PH) 8], 1.50 [d, 3 H, MeP, *J*(PH) 9], 2.3 (s, 3 H, $C_6H_4\mathit{Me}$), 4.79—5.38 (m, 4 H, C_5H_4), 7.2 (m, 9 H, C_6H_4 and Ph)	271 (μ-*C*C_6H_4Me-4), 209 (CO), 163 (C^1, C_6H_4Me-4), 142—128 (C_6H_4, Ph), 103—93 (C_5H_4), 21 (Me-4), 18.9 [d, MeP, *J*(PC) 24], 17.4 [d, MeP, *J*(PC) 24], 0.5 ($SiMe_3$)
(8) [i, k]	0.18 (s, 9 H, $SiMe_3$), 1.42 (m, br, 12 H, MeP), 2.34 (s, 3 H, $C_6H_4\mathit{Me}$), 4.58—5.32 (m, 4 H, C_5H_4), 6.87—7.63 (m, 14 H, C_6H_4, Ph)	215 (CO), 164 (C^1, C_6H_4Me-4), 131—128 (C_6H_4, Ph), 102—94 (C_5H_4), 21 (Me-4), 18.5 [d, MeP, *J*(PC) 22], 17.2 [d, MeP, *J*(PC) 22], 0.5 ($SiMe_3$)
(9) [c, d]	0.24 (s, 9 H, $SiMe_3$), 2.24 (s, 3 H, $C_6H_4\mathit{Me}$), 3.2 (m, 2 H, CH_2), 5.0—5.4 (m, 4 H, C_5H_4), 6.5—7.2 (m, 24 H, C_6H_4 and Ph)	267 (μ-*C*C_6H_4Me-4), 223 (WCO), 212, 205 (CoCO), 163 (C^1, C_6H_4Me-4), 137—128 (C_6H_4, Ph), 102—94 (C_5H_4), 28.4 [t, CH_2, *J*(PC) 23], 21.2 (Me-4), 0.6 ($SiMe_3$)
(10) [g, h, l]	0.36 (s, 18 H, $SiMe_3$), 2.34 (s, 3 H, $C_6H_4\mathit{Me}$), 5.34 (s, 5 H, C_5H_5), 7.0 (m, 4 H, C_6H_4)	259 (μ-*C*C_6H_4Me-4), 233 [WCO, *J*(WC) 154], 213, 212 [$Co(CO)_2$], 200 [$Co(CO)_3$], 159 (C^1, C_6H_4Me-4), 135, 128.1, 127.9 (C_6H_4), 96.5 (*C*$SiMe_3$), 95.5 (C_5H_5), 83 (*C*SiMe), 21 (Me-4), 2.6—2.0 ($SiMe_3$)
(11) [g, h]	1.78, 2.16, 2.26 (s, 9 H, $C_6H_4\mathit{Me}$, COMe), 5.46 (s, 1 H, CH), 5.66 (s, 5 H, C_5H_5), 7.5 (m, 4 H, C_6H_4)	310 [d, μ-*C*C_6H_4Me-4, *J*(RhC) 27], 223.5, 222.1 (WCO), 187.6 (*C*OMe), 184.2 [d, RhCO, *J*(RhC) 73], 155 (C^1, C_6H_4Me-4), 140, 129.3, 128.7 (C_6H_4), 100 (CH), 93 (C_5H_5), 27.4, 26.7 (CO*Me*), 22 (Me-4)
(12) [g, h]	1.96, 2.02 (s, 12 H, COMe), 2.4 (s, 3 H, $C_6H_4\mathit{Me}$-4), 5.42 (s, 2 H, CH), 5.6 (s, 5 H, C_5H_5), 7.40 (m, 4 H, C_6H_4)	302 [t, μ-*C*C_6H_4Me-4, *J*(RhC) 31], 225 [WCO, *J*(WC) 173], 212 [t, μ-CO, *J*(RhC) 44], 189, 185 (*C*OMe), 158 (C^1, C_6H_4Me-4), 139, 129, 127 (C_6H_4), 100 (CH), 94 (C_5H_5), 27 (CO*Me*), 22 (Me-4)

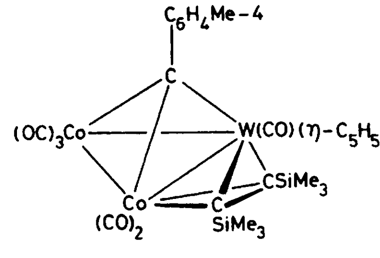
[a] Coupling constants in Hz, all measurements at room temperature unless otherwise stated. [b] Hydrogen-1 decoupled, in p.p.m. to high frequency of $SiMe_4$. [c] ^1H spectrum measured in [$^2H_6$]benzene [d] ^{13}C spectrum measured in [$^2H_2$]dichloromethane. [e] ^{13}C spectrum at −80 °C. [f] Measured in [$^2H_2$]dichloromethane. [g] ^1H spectrum measured in [$^2H_1$]chloroform. [h] ^{13}C spectrum measured in [$^2H_1$]chloroform–CH_2Cl_2. [i] ^{13}C spectrum measured in [$^2H_1$]chloroform. [j] ^{13}C spectrum at −60 °C. [k] ^1H spectrum measured in [$^2H_2$]dichloromethane. [l] ^{13}C spectrum measured at −40 °C.

rence of absorptions in the range 1 890—1 795 cm^{-1} indicates the presence in solution of species with bridging or semi-bridging CO ligands. Similar isomerism is shown [21] by Lewis base derivatives of [$Co_3(\mu_3\text{-}CR)(CO)_9$]. For complexes (2)—(4) and (6)—(8) interconversion between isomers is evidently rapid on the n.m.r. time-scale, since in their ^{13}C n.m.r. spectra only a single resonance is observed for the CO groups, in accord with fast site exchange for these ligands; even at −60 °C for (7). However, in the spectra of (5) and (9) signals corresponding to three CO environments are observed (Table 3), although these room temperature data probably do not correspond to limiting spectra. The resonance in both compounds near δ 220 p.p.m. may be assigned to tungsten-bonded CO and the resonances at *ca.* δ 212 and 205 p.p.m. to CoCO and μ-CO groups.[22,23] The relatively poor solubilities of (5) and (9) inhibited ^{13}C n.m.r. studies at low temperatures.

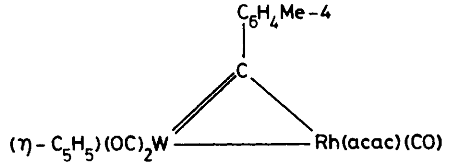
The ^{31}P n.m.r. spectra (Table 2) of the various phosphine derivatives show a single resonance which is devoid of ^{31}P–^{183}W coupling, indicating that the phosphorus atoms are bonded to cobalt. Moreover, the observation of only one signal in the low-temperature spectra of the disubstituted compounds (3) and (8), and in the dppm complexes (5) and (9), confirms that both cobalt atoms are ligated by the phosphine groups, and further indicates that the environments of the phosphorus atoms at the two centres are the same. In the compound [$Co_3(\mu_3\text{-}CMe)(CO)_7(Me_2As\overline{C(CF_2)_2C}AsMe_2)$] an *X*-ray crystallographic study [24] has revealed that the bidentate arsine ligand has replaced two axial carbonyl groups on two of the three cobalt atoms in [$Co_3(\mu_3\text{-}CMe)(CO)_9$]. Moreover, the metal triangle is bridged by three CO ligands, two of the bridges being asymmetric. In view of this study, complexes (5), (6), and (9) in the solid state may have structures similar to [$Co_3(\mu_3\text{-}CMe)(CO)_7(Me_2As\overline{C(CF_2)_2C}AsMe_2)$], as depicted, while for the sake of convenience non-bridging-CO isomers of (2), (3), (4), (7), and (8) are shown.

The ^{13}C n.m.r. spectra of compounds (2), (3), (5), (6), (7), and (9) each show resonances for the μ_3-C atom in the range δ 264—271 p.p.m., as expected.[5] Failure to observe the corresponding signal in the spectra of (4) and

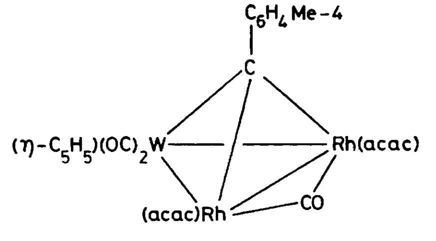
(8) was probably due to insufficient sample in solution, the resonance for μ_3-C being normally of relatively low intensity. An interesting feature of the ^{13}C n.m.r. spectra of (2), (3), (7), and (8) was the observed inequivalence of the two Me groups of the PMe_2Ph ligands (Table 3), which arises because of the chiral nature of the cobalt centres in these complexes. Similar inequivalence is observed in some of the ^1H n.m.r. spectra.



(10)



(11)



(12)

Recently, it has been shown[25] that the cluster compound $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ reacts with the alkyne $Me_3SiC_2SiMe_3$ to give the complex $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}Me_3SiC_2SiMe_3)(\mu\text{-}CO)(CO)_6(\eta\text{-}C_5H_5)]$. An *X*-ray crystallographic study on the latter compound established that the bis(trimethylsilyl)acetylene ligand bridges an Fe-W bond *via* an η^2-bonding mode, and that the tolylidyne ligand remains μ_3-bonded to the Fe_2W triangle, as in the parent complex. In order to establish whether compound (1) would form a similar derivative, its reaction with $Me_3SiC_2SiMe_3$ was investigated.

No reaction occurred between (1) and the alkyne at room temperature in light petroleum as solvent. However, on refluxing the reactants in heptane, the parent cluster was consumed, as revealed by monitoring by i.r. spectroscopy. Dark green-black crystals of complex (10) were isolated. The compound was characterised by microanalysis (Table 1) and a field desorption mass spectrum which revealed a parent ion. The ^{13}C n.m.r. spectrum showed a characteristic resonance for a μ_3-C atom at δ 259 p.p.m. Two signals were observed for the ligated carbon atoms *C*SiMe$_3$ of the alkyne, indicating these two groups are non-equivalent in the structure. Useful structural information was obtained by a variable-temperature study, although ^{13}C n.m.r. data below −40 °C could not be obtained due to the insolubility of

TABLE 4

Atomic positional parameters (fractional co-ordinates) for $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$ (1) *

Atom	*x*	*y*	*z*
W	0.164 2(0)	0.2500	0.239 5(0)
Co	0.074 2(1)	0.355 4(1)	0.119 5(0)
C(1)	0.222 8(8)	0.2500	0.128 6(4)
C(2)	0.350 4(7)	0.2500	0.088 6(4)
C(3)	0.413 8(5)	0.349 9(5)	0.069 3(3)
C(4)	0.536 6(8)	0.351 0(5)	0.033 4(3)
C(5)	0.600 0(8)	0.2500	0.015 2(4)
C(51)	0.733 4(9)	0.2500	−0.023 8(5)
C(01)	0.158 7(10)	0.2500	0.366 6(5)
C(02)	0.091 7(7)	0.346 8(6)	0.343 0(3)
C(03)	−0.024 8(6)	0.308 8(5)	0.307 8(3)
C(001)	0.312 2(6)	0.360 5(5)	0.241 8(3)
O(001)	0.402 4(5)	0.421 4(4)	0.243 9(2)
C(11)	0.130 3(5)	0.490 0(5)	0.151 5(3)
O(11)	0.165 8(4)	0.576 8(3)	0.172 0(2)
C(12)	0.088 7(5)	0.377 5(5)	0.022 5(3)
O(12)	0.100 4(5)	0.391 5(4)	−0.039 2(2)
C(13)	−0.100 8(6)	0.374 2(4)	0.140 2(3)
O(13)	−0.211 4(4)	0.389 1(4)	0.151 7(2)
H(3)	0.351(6)	0.419(5)	0.079(3)
H(4)	0.575(6)	0.420(5)	0.027(3)
H(511)	0.726(8)	0.2500	−0.075(7)
H(512)	0.776(8)	0.328(7)	−0.016(4)
H(01)	0.245(1)	0.2500	0.376(5)
H(02)	0.106(6)	0.431(5)	0.354(3)
H(03)	−0.089(5)	0.357(4)	0.287(3)

* Estimated standard deviations are in parentheses in Tables 4—7.

TABLE 5

Internuclear distances (Å) and angles (°) for $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$ (1)

(*a*) Distances

W–Co	2.672(1)	Co–Co′	2.488(1)
W–C(1)	2.103(7)	Co–C(1)	1.953(6)
W–C(001)	1.981(6)	C(001)–O(001)	1.159(7)
Co–C(11)	1.784(6)	C(11)–O(11)	1.147(7)
Co–C(12)	1.790(5)	C(12)–O(12)	1.142(7)
Co–C(13)	1.816(6)	C(13)–O(13)	1.146(7)
C(1)–C(2)	1.496(10)	C(2)–C(3)	1.386(6)
C(3)–C(4)	1.398(8)	C(4)–C(5)	1.393(7)
C(5)–C(51)	1.519(12)	C(01)–C(02)	1.394(9)
C(02)–C(03)	1.409(9)	C(03)–C(03)′	1.389(12)

(*b*) Angles

Co–W–Co′	55.5(1)	W–Co–Co′	62.3(1)
Co–W–C(1)	46.4(2)	W–Co–C(1)	51.3(2)
Co–Co–C(1)	50.4(3)	Co–C(1)–Co′	79.2(3)
W–C(1)–Co	82.3(2)	Co–W–C(001)	88.0(2)
W–Co–C(11)	92.3(2)	W–Co–C(12)	99.6(2)
W–Co–C(13)	102.5(2)	C(001)–W–C(001)′	82.4(3)
C(1)–W–C(001)	79.0(2)	C(1)–Co–C(11)	107.3(2)
C(1)–Co–C(12)	96.6(3)	C(1)–Co–C(13)	143.6(4)
W–C(001)–O(001)	177.0(5)	Co–C(11)–O(11)	179.7(3)
Co–C(12)–O(12)	178.8(5)	Co–C(13)–O(13)	177.8(5)
W–C(1)–C(2)	135.8(5)	Co–C(1)–C(2)	128.7(3)
C(1)–C(2)–C(3)	121.7(3)	C(3′)–C(2)–C(3)	116.6(7)
C(2)–C(3)–C(4)	122.3(6)	C(3)–C(4)–C(5)	120.5(6)
C(4)–C(5)–C(4)′	117.8(7)	C(4)–C(5)–C(51)	121.1(4)
C(02′)–C(01)–C(02)	110.1(8)	C(01)–C(02)–C(03)	106.3(6)
C(02)–C(03)–C(03)′	108.7(8)		

(10). At room temperature the CO ligands gave rise to a sharp resonance at δ 233 p.p.m., and two broad signals at δ 200 and 212.4 p.p.m. On cooling to −40 °C the band at 212.4 p.p.m. sharpened into two distinct peaks (δ 211.6 and 212.6 p.p.m.), as might be expected for two non-equivalent CO ligands of a $Co(CO)_2$ group. The resonance at 200 p.p.m. remained broad and is assigned to a $Co(CO)_3$ group.[13] The $M(CO)_3$ fragment is known to exhibit dynamic behaviour to very low temperatures, whilst for $M(CO)_2$ groups the fluxional process can be slowed down. Moreover, the sharp resonance at δ 233 p.p.m. is in the region typical for a WCO group.[23] These data are in agreement with the structure shown for (10) which is, therefore, clearly analogous to that of the iron-tungsten compound mentioned above.

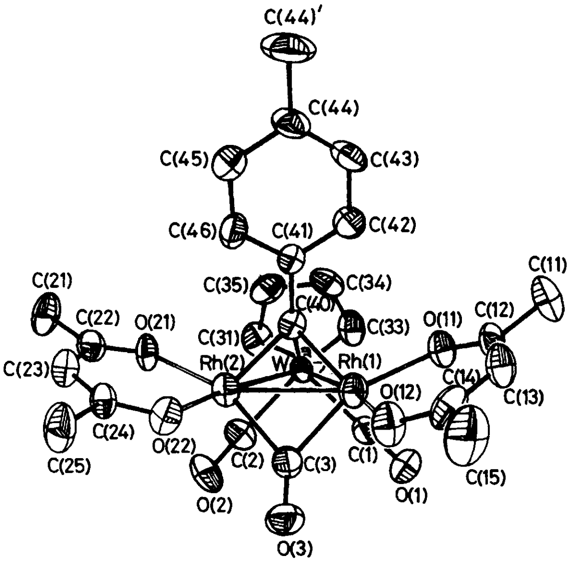


FIGURE 2 Molecular structure of $[Rh_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(acac)_2(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)]$ (12) showing the atom numbering scheme

The synthesis of (1) from $[W{\equiv}CC_6H_4Me\text{-}4(CO)_2(\eta\text{-}C_5H_5)]$ and $[Co_2(CO)_8]$ prompted a study of reactions of the former complex with rhodium compounds having readily replaceable ligands, with the object of obtaining new species with rhodium–tungsten bonds and a bridging μ- or μ_3-CC_6H_4Me-4 group. We have earlier reported[22] the synthesis of the compounds $[RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_4R')(\eta\text{-}C_9H_7)]$ (R' = H or $SiMe_3$) prepared by reacting $[W{\equiv}CC_6H_4Me\text{-}4(CO)_2(\eta\text{-}C_5H_4R)]$ with the indenylrhodium complex $[Rh(CO)_2(\eta\text{-}C_9H_7)]$.

In the present study, the tungsten compound $[W{\equiv}CC_6H_4Me\text{-}4(CO)_2(\eta\text{-}C_5H_5)]$ was found to react rapidly with $[Rh(acac)(CO)_2]$ at room temperature in light petroleum to give the dark purple compound $[RhW(\mu\text{-}CC_6H_4Me\text{-}4)(acac)(CO)_3(\eta\text{-}C_5H_5)]$ (11), analytical and spectroscopic data for which are given in Tables 1—3. The presence of the μ-CC_6H_4Me-4 ligand is clearly revealed from the ^{13}C n.m.r. spectrum which shows a resonance at δ 310 p.p.m. as a doublet signal [J(RhC) 27 Hz]. Carbonyl ligand resonances at δ 184.2, 223.5, and 222.1 p.p.m. may be assigned to RhCO and WCO groups, since the first occurs as a doublet [J(RhC) 73 Hz]. The appearance in the i.r. spectrum of a CO stretching band at 1 881 cm^{-1} suggests that one of the carbonyl groups is semi-bridging.[2]

Reaction of compound (11) with $[Rh(acac)(C_2H_4)_2]$ in dichloromethane affords the dirhodiumtungsten compound $[Rh_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(acac)_2(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)]$ (12). Complex (12) is also produced by reacting $[Rh(acac)(C_2H_4)_2]$ with $[W{\equiv}CC_6H_4Me\text{-}4(CO)_2(\eta\text{-}C_5H_5)]$, but in low yield, and mixed with other products since the reaction is non-stoicheiometric. The ^{13}C n.m.r. spectrum of (12) (Table 3) showed the characteristic resonance for a μ_3-C atom at δ 302 p.p.m., occurring as a triplet signal, due to coupling with two equivalent ^{103}Rh nuclei [J(RhC) 31 Hz]. Moreover, the CO ligand signal at δ 212 p.p.m. was also a triplet [J(RhC) 44 Hz], indicating that this group is bridging the Rh–Rh bond. A band in the i.r. spectrum at 1 825 cm^{-1} (Table 2) supports this contention. Moreover, a bridging CO ligand would result in the rhodium atoms having 16-electron configurations, with the cluster as a whole having 46 valence electrons, or 4 bond pairs to hold the core atoms together. The cluster is thus electronically 'unsaturated' with respect to (1) or the species $[Co_3(\mu_3\text{-}CR)(CO)_9]$ with 50 valence electrons. These properties prompted a single-crystal X-ray diffraction study of (12) to establish firmly the molecular structure.

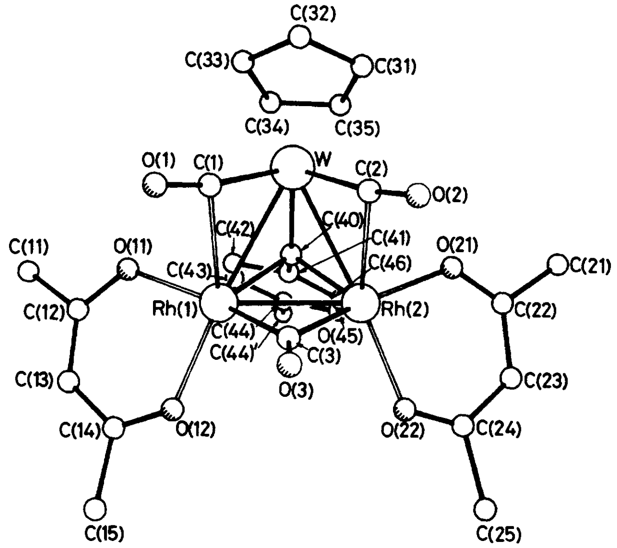


FIGURE 3 The molecular structure of (12) projected onto the plane of the metal atom triangle; the slight deviations from mirror symmetry are evident

The results are illustrated in Figures 2 and 3, the former giving an overall view of the molecule and the latter a projection onto the plane of the metal atom triangle. As expected, the Rh_2W triangle is triply bridged by the tolylidyne ligand, and the acetylacetonate ligands both function as bidentate oxygen donors to the rhodium atoms. The Rh–Rh bond is symmetrically bridged by one of the carbonyl ligands; the other two

TABLE 6

Atomic positional parameters (fractional co-ordinates) for $[\mathrm{Rh_2W}(\mu_3\text{-}\mathrm{CC_6H_4Me}\text{-}4)(\mathrm{acac})_2(\mu\text{-}\mathrm{CO})(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_5})]$ (12)

Atom	*x*	*y*	*z*
W	0.286 64(3)	0.142 71(3)	0.432 14(2)
Rh(1)	0.296 60(6)	0.135 10(7)	0.219 39(5)
Rh(2)	0.340 56(6)	0.338 99(6)	0.281 21(5)
C(1)	0.387 9(8)	−0.000 3(10)	0.360 9(8)
O(1)	0.447 0(8)	−0.094 1(8)	0.332 5(6)
C(2)	0.444 7(8)	0.214 9(11)	0.418 6(7)
O(2)	0.539 7(8)	0.247 5(9)	0.422 8(7)
C(3)	0.453 9(8)	0.207 8(10)	0.201 4(8)
O(3)	0.560 6(7)	0.184 1(9)	0.168 7(7)
O(11)	0.187 5(7)	0.000 2(8)	0.226 0(6)
O(12)	0.334 2(8)	0.136 8(8)	0.058 1(5)
C(11)	0.054 6(13)	−0.123 5(15)	0.178 1(11)
C(12)	0.155 1(10)	−0.036 6(11)	0.147 4(8)
C(13)	0.195 0(11)	−0.002 8(11)	0.044 5(8)
C(14)	0.282 5(12)	0.079 2(11)	0.005 4(8)
C(15)	0.315(2)	0.105(2)	−0.109 4(9)
O(21)	0.298 1(7)	0.476 4(7)	0.374 8(6)
O(22)	0.393 4(7)	0.472 9(7)	0.159 0(5)
C(21)	0.257 7(14)	0.674 2(13)	0.435 8(10)
C(22)	0.300 9(9)	0.590 6(11)	0.350 6(8)
C(23)	0.343 2(10)	0.647 4(11)	0.250 2(9)
C(24)	0.383 6(9)	0.586 5(9)	0.163 0(9)
C(25)	0.427 8(14)	0.669 2(12)	0.061 2(10)
C(40)	0.191 6(8)	0.249 1(9)	0.323 3(6)
C(41)	0.062 4(8)	0.311 0(9)	0.304 4(6)
C(42)	−0.028 3(9)	0.238 1(10)	0.293 9(8)
C(43)	−0.151 8(9)	0.298 6(12)	0.276 2(10)
C(44)	−0.189 7(9)	0.429 6(12)	0.267 4(9)
C(45)	−0.094 8(11)	0.504 1(12)	0.277 5(12)
C(46)	0.029 0(11)	0.441 7(11)	0.291 6(11)
C(44)′	−0.320 8(11)	0.495(2)	0.250 6(15)
C(31)	0.245 7(11)	0.181 2(13)	0.605 0(8)
C(32)	0.277 4(9)	0.051 3(11)	0.604 6(7)
C(33)	0.182 7(11)	0.012 4(11)	0.561 8(8)
C(34)	0.090 6(9)	0.117 6(12)	0.536 4(8)
C(35)	0.127 6(11)	0.222 6(12)	0.563 5(8)
Solvent molecule			
C(51)	−0.090(3)	0.431(3)	−0.003 2(13)
C(52)	−0.111(3)	0.564(3)	−0.027(2)
C(53)	−0.035(3)	0.627(2)	−0.025 6(15)

carbonyl ligands are terminal to the W atom but each is semi-bridging to one of the Rh atoms. Detailed examination of the molecular dimensions (Table 7), however, shows some unexpected differences for a molecule which possesses near-mirror symmetry. Thus the two W–Rh distances are different, 2.809(2) Å to Rh(1) and 2.764(2) Å to Rh(2), though the bridging carbyne is (within the accuracy of this determination) symmetrically bonded: C(40)–Rh(1) 2.030(8), C(40)–Rh(2) 1.994(9), C(40)–W 1.991(8) Å. The Rh–Rh distance is very short at 2.613(2) Å and may be compared with 2.645(1) in $[\mathrm{PtRh_2}(\mu\text{-}\mathrm{CO})_2(\mathrm{CO})(\mathrm{PPh_3})(\eta\text{-}\mathrm{C_5Me_5})_2]$ [26] where there are two bridging carbonyl ligands associated with this bond, with 2.667(2) Å in the corresponding monocation [27] where the extra proton bridges the Pt–Rh(2) bond, and with 2.620(2) Å in $[\mathrm{PtRh_4}(\mu\text{-}\mathrm{CO})_4(\eta\text{-}\mathrm{C_5Me_5})_4]$ where again [27] there are two bridging carbonyls associated with each of the Rh–Rh bonds. It seems, therefore, that the shortness of the Rh–Rh bond is associated with the electronic unsaturation of the molecule, discussed earlier.

Other features of the molecule are as expected, dimensionally, though the rhodium-oxygen bonds are not quite equivalent, those to O(11) and O(21) being shorter than those to O(12) and O(22). The tolyl group is twisted relative to the pseudo-mirror plane of the molecule, probably for reasons of crystal packing, and the axis of the tolylidyne ligand is not perpendicular to the plane of the metal atom triangle (Figure 3). If, however, the molecule is viewed as the transverse addition of a tungsten-carbyne to a dinuclear rhodium species, the 'bend-back' angle of the carbyne ligand would not of necessity orientate this ligand perpendicular to the metal atom triangle. In (12) this angle, W–C(40)–C(41) = 142°, while that to the centroid of the cyclopentadienyl ligand is 116°. The carbonyl ligands on the tungsten atom have W–C–O angles of 171°, in accordance with their mild interaction with the neighbouring rhodium atoms [Rh(1)–C(1) 2.412(9), Rh(2)–C(2) 2.386(9) Å]. As Figure 3 shows, the cyclopentadienyl ring does not conform well with the pseudo-mirror symmetry of the molecule, atoms C(31) and C(35) being considerably further from the 'mirror' plane than are C(33) and C(34). All the carbon atoms are, however, equidistant from the W atom, giving a genuinely η^5 attachment. Whatever the cause of this asymmetry (and it may well be crystal

TABLE 7

Selected * interatomic distances (Å) and angles (°) for $[\mathrm{Rh_2W}(\mu_3\text{-}\mathrm{CC_6H_4Me}\text{-}4)(\mathrm{acac})_2(\mu\text{-}\mathrm{CO})(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_5})]$ (12)

(*a*) Distances

(*i*) Metal triangle and bridging tolylidyne ligand

Rh(1)–Rh(2)	2.613(2)	Rh(1)–C(40)	2.030(8)
W–Rh(1)	2.809(2)	Rh(2)–C(40)	1.994(9)
W–Rh(2)	2.764(2)	W–C(40)	1.991(8)
C(40)–C(41)	1.46(1)	C(44)–C(45)	1.45(2)
C(41)–C(42)	1.41(1)	C(45)–C(46)	1.40(2)
C(42)–C(43)	1.40(1)	C(46)–C(41)	1.38(1)
C(43)–C(44)	1.39(2)	C(44)–C(44)′	1.48(2)

(*ii*) Carbonyl ligands

Rh(1)–C(1)	2.412(9)	Rh(2)–C(2)	2.386(9)
W–C(1)	1.973(9)	W–C(2)	1.978(10)
Rh(1)–C(3)	1.967(10)	Rh(2)–C(3)	1.988(10)
C(1)–O(1)	1.164(12)	C(2)–O(2)	1.157(14)
C(3)–O(3)	1.149(11)		

(*iii*) Rh–acetylacetonate ligands

Rh(1)–O(11)	2.029(8)	Rh(2)–O(21)	2.010(8)
O(11)–C(12)	1.287(14)	O(21)–C(22)	1.233(13)
C(12)–C(11)	1.53(2)	C(22)–C(21)	1.51(2)
C(12)–C(13)	1.373(14)	C(22)–C(23)	1.417(14)
C(13)–C(14)	1.40(2)	C(23)–C(24)	1.378(15)
C(14)–C(15)	1.497(15)	C(24)–C(25)	1.558(15)
C(14)–O(12)	1.26(2)	C(24)–O(22)	1.219(15)
Rh(1)–O(12)	2.100(7)	Rh(2)–O(22)	2.083(7)

(*iv*) W–cyclopentadienyl ligand

W–C(31)	2.337(11)	W–C(34)	2.369(9)
W–C(32)	2.337(9)	W–C(35)	2.360(10)
W–C(33)	2.329(11)	C–C(mean)	1.40

(*b*) Angles

Rh(1)–Rh(2)–W	62.9(1)	Rh(2)–Rh(1)–W	61.2(1)
Rh(1)–W–Rh(2)	55.9(1)	Rh(1)–C(40)–W	88.6(3)
Rh(2)–C(40)–W	87.8(3)	Rh(1)–C(40)–Rh(2)	81.0(3)
Rh(1)–C(40)–C(41)	117.8(6)	Rh(2)–C(40)–C(41)	121.5(6)
W–C(40)–C(41)	141.7(5)	Rh(1)–C(3)–Rh(2)	82.7(3)
W–Rh(1)–O(11)	99.1(2)	W–Rh(2)–O(21)	96.3(2)
O(11)–Rh(1)–O(12)	88.9(3)	O(21)–Rh(2)–O(22)	89.0(3)
W–C(1)–O(1)	170.5(8)	W–C(2)–O(2)	171.0(8)

* A complete list of bond lengths and angles has been deposited (SUP 23232).

packing, even though there are no singularly short intermolecular distances), there is presumably a direct relationship between the asymmetry of the C_5H_5 position and the difference in the two W–Rh bond lengths. A not dissimilar distortion was found[28] in the molecular structure of $[Pt_2Ru(\mu\text{-}CO)_3(CO)_3(PMePh_2)_3]$.

EXPERIMENTAL

Analytical data and yields for the new compounds are given in Table 1. 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, with solvents dried and distilled under nitrogen prior to use. The n.m.r. measurements were made with JEOL-JNM FX90Q and FX200 instruments, and i.r. spectra recorded with Perkin-Elmer 257 spectrometers. The compounds $[Rh(acac)(C_2H_4)_2]$ and $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_4SiMe_3)]$ were prepared by literature methods.[5, 29]

Synthesis of $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$ (1).—The compound $[W{\equiv}CC_6H_4Me\text{-}4(CO)_2(\eta\text{-}C_5H_5)]$ (0.41 g, 1 mmol) in light petroleum (20 cm³) reacted vigorously with $[Co_2(CO)_8]$ (0.34 g, 1 mmol), with CO evolution and formation of a dark green solution. After stirring (1 h), the solution was cooled to −78 °C precipitating green *crystals* of $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$ (1) (0.66 g) in quantitative yield.

Reactions of $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$ (1).—(*a*) Dimethylphenylphosphine (0.71 mmol) was added to a diethyl ether (20 cm³) solution of (1) (0.49 g, 0.71 mmol). After stirring (24 h), solvent was removed *in vacuo* and the green residue dissolved in dichloromethane–light petroleum (2 : 5) and chromatographed on alumina. Elution with the same solvent mixture gave a small amount of (1) and, after evaporation of solvent, dark green *microcrystals* of $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_7(PMe_2Ph)(\eta\text{-}C_5H_5)]$ (2) (0.25 g).

(*b*) A diethyl ether (20 cm³) solution of (1) (0.37 g, 0.54 mmol) was treated with PMe_2Ph (0.15 g, 1.1 mmol) and the mixture stirred (24 h). Since free PMe_2Ph could be detected, the reactants were refluxed (3 h). Solvent was removed *in vacuo* and the residue dissolved in dichloromethane–light petroleum (2 : 5) and chromatographed on an alumina column. A brown band was eluted which after evaporation of solvent gave brown *crystals* of $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$ (3) (0.28 g).

(*c*) Compound (1) (0.66 g, 0.86 mmol) in diethyl ether (20 cm³) was treated with excess $P(OMe)_3$ (0.5 cm³), and the mixture refluxed (3 h). Solvent was removed *in vacuo* and the residue dissolved in dichloromethane–light petroleum and chromatographed, eluting a very dark green band. Removal of solvent yielded black *crystals* of $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ (4) (0.46 g).

(*d*) Compound (1) (0.40 g, 0.58 mmol) in diethyl ether (40 cm³) was treated with dppm (0.22 g, 0.58 mmol) and the mixture stirred (24 h). After removal of solvent, the residue was chromatographed. Elution with dichloromethane–light petroleum (1 : 1) gave after evaporation of solvent dark green *microcrystals* of $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(dppm)(\eta\text{-}C_5H_5)]$ (5) (0.35 g).

(*e*) Compound (1) (0.50 g, 0.42 mmol) in diethyl ether (20 cm³) was treated with diars (3.4 cm³ of a 0.21 mol dm⁻³ light petroleum solution), and the mixture stirred (15 h), and then refluxed (2 h). Solvent was removed *in vacuo*, and the residue dissolved in dichloromethane–light petroleum (1 : 2) and chromatographed. A brown band was eluted; from the solution black *crystals* of $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(diars)(\eta\text{-}C_5H_5)]$ (6) (0.49 g) were obtained.

(*f*) Compound (1) (0.62 g, 0.89 mmol) in light petroleum (20 cm³) was treated with $Me_3SiC_2SiMe_3$ (3.7 mmol), but after 24 h with stirring, i.r. spectroscopy revealed little reaction. The solvent was removed *in vacuo* and replaced with heptane (20 cm³) and the mixture refluxed (24 h). The dark green solution was evaporated and the residue chromatographed (dichloromethane–light petroleum, 1 : 3). The dark green solution so obtained was reduced in volume and cooled to give *crystals* of the compound $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}Me_3SiC_2SiMe_3)(CO)_6(\eta\text{-}C_5H_5)]$ (10) (0.45 g).

Reactions of $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_4SiMe_3)]$.—(*a*) Green *crystals* of the compound $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_7(PMe_2Ph)(\eta\text{-}C_5H_4SiMe_3)]$ (7) (0.11 g) were isolated following chromatography of the reaction mixture obtained by treating $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_4SiMe_3)]$ (0.35 g, 0.46 mmol) in diethyl ether (20 cm³) with PMe_2Ph (0.46 mmol, 1.3 cm³ of a 0.37 mol dm⁻³ light petroleum solution).

(*b*) Similarly, brown *crystals* of the complex $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(PMe_2Ph)_2(\eta\text{-}C_5H_4SiMe_3)]$ (8) (0.25 g) were obtained by reacting $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_4SiMe_3)]$ (0.53 g, 0.69 mmol) in diethyl ether (20 cm³) with PMe_2Ph (1.4 mmol, 3.9 cm³ of a 0.36 mol dm⁻³ solution in light petroleum (1 : 2)).

(*c*) Addition of dppm (0.29 g, 0.71 mmol) to $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_4SiMe_3)]$ (0.54 g, 0.71 mmol) in diethyl ether (20 cm³) afforded black *crystals* of $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(dppm)(\eta\text{-}C_5H_4SiMe_3)]$ (9) (0.30 g) after chromatography, eluting the product with dichloromethane–light petroleum (1 : 2).

Synthesis of Rhodium–Tungsten Complexes.—(*a*) A light petroleum (15 cm³) solution of $[Rh(acac)(C_2H_4)_2]$ was treated with a stream of CO gas to generate $[Rh(acac)(CO)_2]$. The compound $[W{\equiv}CC_6H_4Me\text{-}4(CO)_2(\eta\text{-}C_5H_5)]$ (0.41 g, 1 mmol) was added to the suspension which rapidly evolved CO. The mixture was stirred (1 h) and a dark solid was precipitated which was collected and washed with light petroleum (2 × 2 cm³ at 0 °C) and dried *in vacuo* to give *microcrystals* of the complex $[RhW(\mu\text{-}CC_6H_4Me\text{-}4)(acac)(CO)_3(\eta\text{-}C_5H_5)]$ (11) (0.45 g).

(*b*) A solution of (11) (0.64 g, 1 mmol) and $[Rh(acac)(C_2H_4)_2]$ (0.26 g, 1 mmol) in dichloromethane (20 cm³) was refluxed for 4 h. The resulting dark purple-brown solution was concentrated *in vacuo* to *ca.* 4 cm³, and addition of light petroleum (*ca.* 5 cm³) afforded black *crystals* of $[Rh_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(acac)_2(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)]$ (12) (0.57 g).

Crystal Structure Determinations.—(*a*) $[Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$ (1). Crystals of (1) grow as ill-formed dark green prisms of poor diffracting power. Intensities were collected at 200 K from a crystal of dimensions 0.40 × 0.10 × 0.40 mm in the range $2.9 \leqslant 2\theta \leqslant 40°$. Of the 2 474 independent intensities measured on a Syntex $P2_1$ four-circle diffractometer, 1 565 for which $(F_o) > 4.0\sigma(F_o)$ were used for the solution and refinement of the structure. Check reflections $2\bar{1}3$ and 042 were remeasured every 50 reflections and showed no significant decay over the 157 h of data collection. Correction was made for Lorentz, polarisation, and *X*-ray absorption effects.

Crystal data for (1). $C_{21}H_{12}Co_2O_8W$, $M = 693.8$, Orthorhombic, $a = 10.067(13)$, $b = 11.806(26)$, $c = 18.203(10)$ Å, $U = 2\,163(5)$ Å³, $Z = 4$, $D_c = 1.97$ g cm⁻³, $F(000) = 1\,320$, space group *Pcmn* (non-standard setting of *Pnma*, no. 62), Mo-K_α X-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 65.8 cm^{-1}.

As explained in the Introduction, the quantitative synthesis described above was devised only after the structure had been determined by X-ray diffraction. In the first instance it was not known whether the crystals contained tungsten and/or platinum and/or cobalt or whether any phosphine ligands were present. A Patterson synthesis showed vectors and peak heights which could be interpreted (given the crystal symmetry) on the basis of a $PtCo_2$ or a WCo_2 triangle of metal atoms located astride a crystallographic mirror plane. Electron-density difference maps phased on $PtCo_2$ revealed all the 'light' atoms of the structure, including hydrogen atoms, and from the disposition of these and the electron count it became clear that the heavy atom was indeed tungsten and not platinum. Substitution of W for Pt in the least-squares refinement of the structure gave much more realistic thermal parameters for the heavy atom than had previously been obtained. Refinement by full-matrix least squares converged at R 0.025 (R' 0.027) and a final electron-density difference synthesis showed no peaks >0.3 or <-0.3 e Å^{-3}. Individual weights were ascribed according to the scheme $w = 0.870[\sigma^2(F_o) + 0.0012|F_o|^2]^{-1}$. Anisotropic thermal parameters were used for all non-hydrogen atoms. Scattering factors were from ref. 30; those for W and Co were also corrected for the effects of anomalous dispersion.[31] All computations were carried out on the South Western Universities' Computer Network with the SHELX system of programs.[32]

(*b*) $[Rh_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(acac)_2(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)]\cdot\frac{1}{2}C_6D_6$ (12). Crystals of (12) grow as black rhombs. Intensities were collected at 293 K from a crystal of dimensions 0.40 × 0.28 × 0.25 mm in the range $2.9 \leqslant 2\theta \leqslant 60°$. This particular crystal had grown from C_6D_6 solution in an n.m.r. tube and was subsequently found to contain $\frac{1}{2}C_6D_6$ of crystallisation. Of the 7 102 independent intensities measured on a Nicolet $P3m$ diffractometer, 5 897 for which $I \geqslant 4.0\sigma(I)$ were used for the solution and refinement of the structure. Check reflections $1\bar{4}\bar{5}$ and $1\bar{4}3$ were remeasured every 50 reflections and showed no significant decay over the 218 h of the data collection. The usual corrections were applied, including an empirical absorption correction.[33] Four very intense reflections ($\bar{1}\bar{1}2$, $\bar{3}02$, $3\bar{2}2$, and $\bar{4}03$) were omitted from the data set.

Crystal data for (12). $C_{26}H_{26}O_7Rh_2W\cdot\frac{1}{2}C_6D_6$, $M = 909.7$, Triclinic, $a = 10.756(8)$, $b = 10.805(6)$, $c = 13.215(13)$ Å, $\alpha = 81.32(7)$, $\beta = 80.44(7)$, $\gamma = 78.60(6)°$, $U = 1\,473(2)$ Å^3, $Z = 2$, $D_c = 2.05$ g cm^{-3}, $F(000) = 846$, space group $P\bar{1}$ (no. 2), μ(Mo-K_α) = 51.1 cm^{-1}.

The structure was solved by heavy-atom methods and was refined by blocked-cascade least squares with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included at calculated positions with an isotropic thermal parameter for each H atom equal to 1.2 times that of the attached C atom. Individual weights were ascribed according to the scheme $w = [\sigma^2(F_o) + 0.0029|F_o|^2]^{-1}$. Scattering factors and corrections for anomalous dispersion were from ref. 30. Refinement converged at R 0.057 (R' 0.061), after the incorporation of half a molecule of C_6D_6 (astride the centre of inversion at $0\frac{1}{2}0$), found from electron-density difference syntheses. All calculations were carried out within the laboratory on an 'Eclipse' Data General Minicomputer with the 'SHELXTL' system of programs.[33] The results for complex (1) are summarised in Tables 4 and 5, for (12) in Tables 6 and 7. Observed and calculated structure factors for (1) and (12), hydrogen atom co-ordinates for (12), and all thermal parameters are given in Supplementary Publication No. SUP 23232 (54 pp.).*

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