Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 24.[1] Complexes of the Pentamethylcyclopentadienylcopper Group and the Crystal Structures of the Compounds $[CuPtW(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ and $[CuRh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_3]$ *

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Treatment of copper(I) chloride with $Li(C_5Me_5)$ in tetrahydrofuran at low temperatures affords a reagent which is a useful source of the $Cu(\eta\text{-}C_5Me_5)$ fragment in syntheses. The preparation of the compounds $[CuW\{\mu\text{-}C(OMe)R\}(CO)_5(\eta\text{-}C_5Me_5)]$, $[Cu_2W(\mu_3\text{-}CR)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)_2]$, $[CuPtW(\mu_3\text{-}CR)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$, $[Cu_2PtW_2(\mu_3\text{-}CR)_2(CO)_4(\eta\text{-}C_5H_5)_2(\eta\text{-}C_5Me_5)_2]$ ($R = C_6H_4Me\text{-}4$), $[CuPt(\mu\text{-}PhC_2Ph)(PMe_3)_2(\eta\text{-}C_5Me_5)]$, and $[CuRh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_3]$ is described, and spectroscopic data (i.r. and n.m.r.) for the new species are reported and discussed. Single-crystal *X*-ray diffraction studies have been carried out on the compounds $[CuPtW(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ and $[CuRh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_3]$. In the former compound, the μ-CCuPtW core atoms adopt a butterfly configuration with an angle of fold of 90.6° between the C,W,Pt and C,W,Cu planes. The Cu $\cdots$ Pt separation [2.807(3) Å] implies little or no metal–metal bonding between these centres. The tungsten atom carries an $\eta\text{-}C_5H_5$ group and two CO ligands, one of which semi-bridges [W–C–O 162(2)°] the Pt–W bond [2.779(2) Å]. The C_5Me_5 ligand on copper is η^5-bonded to the metal, and the Cu–W distance is 2.648(3) Å. The structure of $[CuRh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_3]$ is based on a triangle of metal atoms which, however, proved to be positionally disordered. The data obtained are limited, but the mean metal–metal separation is 2.56(1) Å and the two CO groups are tilted in a way which implies semi-triply bridging behaviour. The important feature that the C_5Me_5 ligand on copper is η^5-co-ordinated is confirmed.

The concept of regarding an organotransition-metal complex as being contructed from metal–ligand fragments and organic groups with similar frontier orbitals[2] has been a useful guideline for the preparation of a variety of compounds. In our hands, the isolobal model has led *inter alia* to the discovery of several new routes to compounds containing heteronuclear metal–metal bonds.[3–8] Metal–ligand fragments with bonding capabilities similar to methylene or carbene are especially useful as building blocks in organometallic syntheses. In this context the groups $Cr(CO)_2(\eta\text{-}C_6Me_6)$, $Mn(CO)_2(\eta\text{-}C_5H_5)$, $Fe(CO)_4$, $Co(CO)(\eta\text{-}C_5Me_5)$, and $Ni(PR_3)_2$, all involving elements of the first transition series, have been successfully used as precursors to species with bonds between these elements and other transition metals. We became interested in extending the above chromium to nickel series to copper, especially as there are relatively few compounds known having bonds between copper and any transition element.[9] A copper species isolobal with CH_2 might be an important reagent for preparing complexes with metal–metal bonds involving this element. This requirement could be met by either a cyclopentadienylcopper or a pentamethylcyclopentadienylcopper group since such fragments, formally ML_3 d^{10} ($M = Cu$, $L_3 = \eta\text{-}C_5H_5$ or $\eta\text{-}C_5Me_5$), have two electrons to distribute between two frontier orbitals of σ and π symmetry.[2] Although a few compounds containing $Cu(\eta\text{-}C_5H_5)$ groups have been prepared[10] they do not involve bonds between copper and other metals. Moreover, the now well established superiority of $\eta\text{-}C_5Me_5$ *versus* $\eta\text{-}C_5H_5$ as a ligand prompted us to direct our attention to the $Cu(\eta\text{-}C_5Me_5)$ moiety. A preliminary account of some of our results has been given.[11]

Results and Discussion

Addition of copper(I) chloride to a tetrahydrofuran (thf) suspension of $Li(C_5Me_5)$ at −78 °C affords a highly reactive dark yellow reagent presumed to be the complex $[Cu(thf)(\eta\text{-}C_5Me_5)]$. It is possible that this thermally unstable solution contains species with C_5Me_5 groups σ bonded to copper. Alternatively, compounds with copper–copper bonds might be present. One possibility in the latter category is the complex $[Cu_2(\eta\text{-}C_5Me_5)_2]$ which is isolobal with the compounds $[M_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ (M = Co or Rh).[12] However, we believe the formation of $[Cu(thf)(\eta\text{-}C_5Me_5)]$ to be more likely. Cotton and Marks[10] have reported a series of complexes $[CuL(\eta\text{-}C_5H_5)]$ [$L = PR_3$ (R = Ph, Et, Bu^n, or OMe), CNMe, or CO], and *X*-ray diffraction studies on the two compounds $[Cu(PR_3)(\eta\text{-}C_5H_5)]$ (R = Et or Ph) have established that the cyclopentadienyl ligands are η^5 bonded.[13,14] There thus seems little reason to doubt the existence of $[Cu(thf)(\eta\text{-}C_5Me_5)]$, which might well be thermally very unstable, as are the species $[CuL(\eta\text{-}C_5H_5)]$ (L = CO or CNBu^t).[10]

Whatever the nature of the product obtained from $Li(C_5Me_5)$ and CuCl in thf, it is a ready source of the $Cu(\eta\text{-}C_5Me_5)$ fragment in a variety of syntheses. Reactants were added at −78 °C, and the mixtures allowed to warm slowly to room temperature. Thus, addition of PPh_3 gave an air-sensitive compound (1), analogous to the previously reported complex $[Cu(PPh_3)(\eta\text{-}C_5H_5)]$.[10] Of more interest was the reaction of $[Cu(thf)(\eta\text{-}C_5Me_5)]$ with the tungsten–carbene complex $[W\{=C(OMe)R\}(CO)_5]$ ($R = C_6H_4Me\text{-}4$) which afforded compound (2) as air-stable magenta crystals, characterised by

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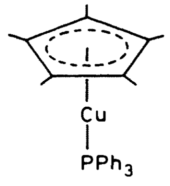
* 2,3-μ-Carbonyl-2-carbonyl-2-η-cyclopentadienyl-1-η-pentamethylcyclopentadienyl-μ_3-*p*-tolylmethylidyne-3,3-bis(trimethylphosphine)copperplatinumtungsten(*Cu–W, W–Pt*) and di-μ_3-carbonyl-tris(η-pentamethylcyclopentadienyl)-*triangulo*-copperdirhodium.

Supplementary data available (No. SUP 23917, 37 pp.): thermal parameters, H-atom co-ordinates, complete bond lengths and angles, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.



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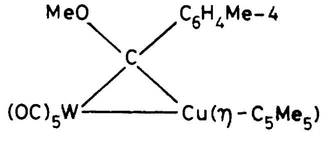

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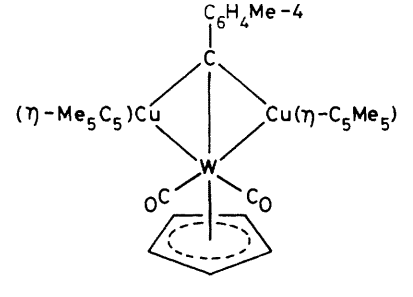

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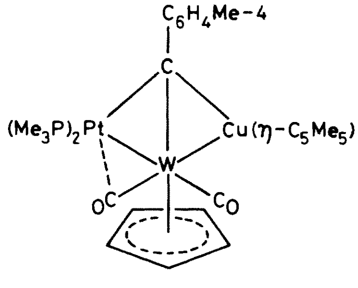

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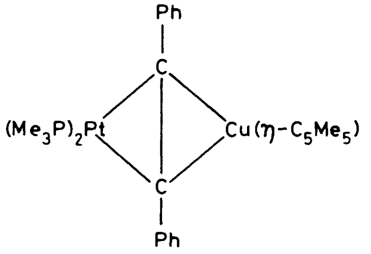

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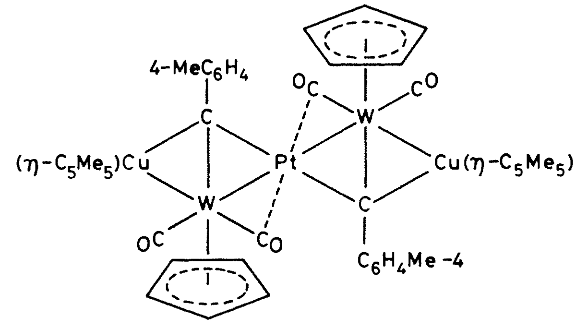

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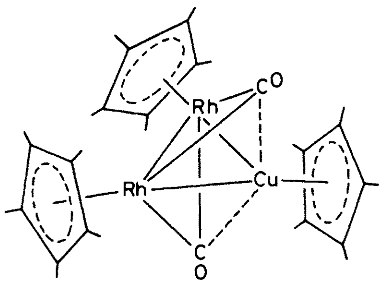

(7)

microanalysis and by observation of a molecular ion in the mass spectrum (Table 1). The n.m.r. data for (2) (Table 2) are in accord with the structure proposed. In particular, the ^{13}C-{^1H} n.m.r. spectrum shows a resonance for the bridging carbon nucleus of the alkylidene ligand at δ 231.5 p.p.m. This shift is in the region expected. For example in the ^{13}C-{^1H} spectrum of the isolobal compound [PtW{μ-C(OMe)R}(CO)$_5$-(PMe$_3$)$_2$] the corresponding signal is at δ 204 p.p.m.[5b]

Several ' carbene-like ' metal–ligand fragments add to the C≡W bond in [W(≡CR)(CO)$_2$(η-C$_5$H$_5$)] to give products with metal–metal bonds bridged by the tolylmethylidyne group.[3,4] The reaction between the new copper reagent and the *p*-tolylmethylidynetungsten compound was, therefore, studied. Using an excess of the copper compound, the dicopper-tungsten complex (3) was produced, and characterised in the usual way (Table 1). There was no evidence for formation of the dimetal compound [CuW(μ-CR)(CO)$_2$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)] which was probably a transient species which readily adds another Cu(η-C$_5$Me$_5$) fragment. Nevertheless, formation of the trimetal compound (3) is in contrast with previous observations with certain other metal–ligand groups which, even when used in excess, react with [W(≡CR)(CO)$_2$(η-C$_5$H$_5$)] to give dimetal rather than trimetal compounds.[8] The presence of the μ$_3$-CR group in compound (3) is clearly indicated by the resonance at δ 275.5 p.p.m. in the ^{13}C-{^1H} n.m.r. spectrum.

The isolobal relationship between the groups Cu(η-C$_5$Me$_5$) and Pt(PMe$_3$)$_2$ is well illustrated by the synthesis of compounds (4) and (5), which were obtained by treating [PtW(μ-CR)-(CO)$_2$(PMe$_3$)$_2$(η-C$_5$H$_5$)] and [Pt(PhC$_2$Ph)(PMe$_3$)$_2$], respectively, with [Cu(thf)(η-C$_5$Me$_5$)]. Microanalytical (Table 1) and n.m.r. (Table 2) data for (4) and (5) were as expected for the structures shown.

The structure of compound (5) is related to that of several previously described diplatinum compounds [Pt$_2$(μ-alkyne)L$_4$] (L = PR'$_3$ or L$_2$ = cyclo-octa-1,5-diene).[15] The ^{31}P-{^1H} n.m.r. spectrum showed a resonance at δ −31.7 p.p.m. [*J*(PtP) 3 408 Hz]. The ^{13}C-{^1H} n.m.r. spectrum (Table 2) had a deceptively simple quintet signal (AA'X) pattern at δ 96.2 [*J*(PtC) 231 Hz] for the ligated carbon atoms of the bridging alkyne group. The corresponding signal for the contact car-

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

Compound [b]	M.p. [c] (θ_c/°C)	Colour	Yield (%)	$\tilde{\nu}_{max.}$(CO) [d]/cm^{-1}	Analysis (%) C	Analysis (%) H
(1) [Cu(PPh$_3$)(η-C$_5$Me$_5$)] [e]		Pale yellow	38		73.0 (72.1)	6.5 (6.7)
(2) [CuW{μ-C(OMe)R}(CO)$_5$(η-C$_5$Me$_5$)] [f]	110	Magenta	51	2 065s, 1 990m, 1 962s, 1 942vs, 1 906vw	44.0 (43.9)	3.8 (3.8)
(3) [Cu$_2$W(μ$_3$-CR)(CO)$_2$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)$_2$]	138	Violet	50	1 934m, 1 855s	52.0 (52.2)	5.4 (5.2)
(4) [CuPtW(μ$_3$-CR)(CO)$_2$(PMe$_3$)$_2$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)]	145	Red-black	62	1 906s, 1 816m(br)	38.9 (39.0)	4.9 (4.7)
(5) [CuPt(μ-PhC$_2$Ph)(PMe$_3$)$_2$(η-C$_5$Me$_5$)]	90	Yellow	45		49.1 (49.8)	6.1 (5.9)
(6) [Cu$_2$PtW$_2$(μ$_3$-CR)$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$(η-C$_5$Me$_5$)$_2$]	114	Red-brown	51	1 934s [g], 1 919s, 1 875vs	42.6 (42.6)	4.4 (3.8)
(7) [CuRh$_2$(μ-CO)$_2$(η-C$_5$Me$_5$)$_3$]	200	Deep blue	46	1 728	52.2 (52.6)	6.2 (6.2)

[a] Calculated values are given in parentheses. [b] R = C$_6$H$_4$Me-4. [c] With decomposition. [d] In pentane, unless otherwise stated. [e] Parent ion in mass spectrum at *m/e* 460. [f] Parent ion in mass spectrum at *m/e* 656. [g] In Nujol.

Table 2. Hydrogen-1 and ^{13}C-{^{1}H} n.m.r. data [a]

Compound [b]	^{1}H (δ)	^{13}C (δ)
(2)	1.60 [c] (s, 15 H, C$_5$Me$_5$), 1.96 (s, 3 H, Me-4), 3.52 (s, 3 H, OMe), 7.0 [(AB)$_2$ quartet, 4 H, C$_6$H$_4$, *J*(AB) 8]	231.5 (μ-C), 202.2 [1 CO, *J*(WC) 134], 197.0 [4 CO, *J*(WC) 122], 155.4—127.0 (C$_6$H$_4$), 108.3 (*C*$_5$Me$_5$), 65.1 (OMe), 21.2 (Me-4), 9.4 (C$_5$*Me*$_5$)
(3)	1.92 (s, 30 H, C$_5$Me$_5$), 2.08 (s, 3 H, Me-4), 4.72 (s, 5 H, C$_5$H$_5$), 6.84 (s, 4 H, C$_6$H$_4$)	275.5 (μ$_3$-C), 213.9 [CO, *J*(WC) 166], 158.7—129.7 (C$_6$H$_4$), 107.8 (*C*$_5$Me$_5$), 90.3 (*C*$_5$H$_5$), 21.3 (Me-4), 10.7 (C$_5$*Me*$_5$)
(4)	0.97 [d, 9 H, MeP, *J*(PH) 9, *J*(PtH) 37], 1.43 [d, 9 H, MeP, *J*(PH) 8, *J*(PtH) 20], 2.13 (s, 15 H, C$_5$Me$_5$), 2.22 (s, 3 H, Me-4), 4.87 (s, 5 H, C$_5$H$_5$), 6.90 (s, 4 H, C$_6$H$_4$)	266.5 [d] [d, μ$_3$-C, *J*(PC) 61, *J*(PtC) 544], 222.8 (CO), 213.2 (CO), 164.2—126.0 (C$_6$H$_4$), 104.8 (*C*$_5$Me$_5$), 90.7 (C$_5$H$_5$), 21.0 (Me-4), 19.5 [d, MeP, *J*(PC) 29], 18.6 [d, MeP, *J*(PC) 24], 11.9 (C$_5$*Me*$_5$)
(5)	1.20 [d, 18 H, MeP, *J*(PH) 8, *J*(PtH) 28], 2.13 (s, 15 H, C$_5$Me$_5$), 7.0—7.4 (m, 10 H, Ph)	129.3 [t, AA′X, C^1(Ph), *J*(CP) + *J*(CP′) 28], 128.0—125.3 (Ph), 102.4 (*C*$_5$Me$_5$), 96.2 [five-line m, AA′X, *C*Ph, *J*(CP) ±75, *J*(CP′) ∓5, *J*(PP) 25, *J*(PtC) 231], 21.2 [t, AA′X, MeP, *J*(CP) + *J*(CP′) 28], 11.6 (C$_5$*Me*$_5$)
(6) [e]	2.05 (br, 36 H, C$_5$Me$_5$, Me-4), 4.96 (s, br, 10 H, C$_5$H$_5$), 7.04 [(AB)$_2$ quartet, 8 H, C$_6$H$_4$, *J*(AB) 8]	272.9 (μ$_3$-C), 217.2 (CO), 212.1 (CO), 154.0 [C^1(C$_6$H$_4$)], 106.8 (*C*$_5$Me$_5$), 90.8 (*C*$_5$H$_5$), 11.3 (C$_5$*Me*$_5$)
(7)	1.80 (s, 15 H, CuC$_5$Me$_5$), 1.68 (s, 30 H, RhC$_5$Me$_5$)	241.5 [f] [t, CO, *J*(RhC) 44], 105.8 (*C*$_5$Me$_5$Cu), 100.4 (br, *C*$_5$Me$_5$Rh), 10.9 (C$_5$*Me*$_5$Cu), 9.4 (C$_5$*Me*$_5$Rh)

[a] Measured in [^{2}H$_6$]benzene at room temperature, unless otherwise stated. Chemical shifts (δ) in p.p.m., and for ^{13}C-{^{1}H} these are relative to SiMe$_4$, positive values representing shifts to high frequency. Coupling constants are in Hz. [b] R = C$_6$H$_4$Me-4. [c] Measured in [^{2}H$_8$]toluene. [d] Signal for μ$_3$-*C*R measured at −70 °C in [^{2}H$_8$]toluene. [e] Hydrogen-1 and ^{13}C-{^{1}H} spectra measured at −30 °C in [^{2}H$_8$]toluene. Signals for C$_6$H$_4$Me group in ^{13}C spectrum hidden under solvent peaks. [f] Measured at −50 °C in [^{2}H$_8$]toluene.

bons of the alkyne in [Pt$_2$(μ-PhC$_2$Ph)(PMe$_3$)$_4$], also a quintet, occurs at 80.8 p.p.m., with *J*(PtC) 278 Hz.[15]

Compound (4) was structurally characterised by an *X*-ray diffraction study described below. However, the presence of the μ$_3$-CR group was clearly indicated by the doublet signal [*J*(PC) 61 Hz] at 266.5 p.p.m. in the ^{13}C-{^{1}H} n.m.r. spectrum. The observation of ^{195}Pt satellite peaks [*J*(PtC) 544 Hz] is also characteristic for a *C*R ligand bridging bonds between platinum and other metals. Thus in the ^{13}C-{^{1}H} n.m.r. spectrum of [Pt$_2$W(μ$_3$-CR)(CO)$_4$(PMe$_2$Ph)$_2$(η-C$_5$H$_5$)] the corresponding ^{195}Pt–^{13}C coupling is 570 Hz.[16] The ^{1}H n.m.r. spectrum of compound (4), in addition to showing resonances for the C$_5$H$_5$ and C$_5$Me$_5$ ligands, had signals corresponding to PMe$_3$ groups in two different environments. The ^{31}P-{^{1}H} n.m.r. spectrum confirmed the latter conclusion. Two doublet resonances were observed at δ −20.16 [*J*(PP) 5, *J*(PPt) 4 211] and at −29.18 p.p.m. [*J*(PP) 5, *J*(PPt) 2 720 Hz]. The magnitude of the ^{195}Pt–^{31}P coupling on the signal at higher frequency is as expected for the PMe$_3$ ligand transoid to the Pt–W bond.

The results of the *X*-ray diffraction study on compound (4) are summarised in Table 3, and the structure is shown in Figure 1 with the atom numbering scheme. The core atoms Cu, Pt, W, and C adopt a butterfly configuration with Cu and Pt at the wingtips. The Cu ··· Pt separation [2.807(3) Å] is longer than the sum (*ca.* 2.5 Å) of the covalent radii; hence there can be little direct Cu–Pt bonding. A similar situation occurs in the complexes [Pt$_2$(μ-alkyne)L$_4$] where the Pt ··· Pt distances are also too long for significant metal–metal bonding.[15] In compound (4) the RC≡W(CO)$_2$(η-C$_5$H$_5$) group plays the role of an alkyne, leading to a Cu ··· Pt separation set by the bonding requirements of the bridging ligand, which reflect the use of its two orthogonal π orbitals to bond the Pt(PMe$_3$)$_2$ and Cu(η-C$_5$Me$_5$) fragments. In accord with this, the angle of fold between the two planes C,W,Pt and C,W,Cu is 90.6°.

The carbyne-carbon C lies 1.2 Å above the Cu,Pt,W plane, and the tolyl group is virtually perpendicular (89°) to this plane. The C–W distance [2.03(2) Å] may be compared with the μ-C–W distances in [PtW(μ-CR)(CO)$_2$(PMe$_2$Ph)$_2$(η-C$_5$H$_5$)] [1.967(6) Å][3] and in [Pt$_2$W(μ$_3$-CR)(CO)$_4$(PMePh$_2$)$_2$(η-C$_5$H$_5$)] [2.04(4) Å].[16] The P$_2$Pt moiety in compound (4) [P(1)–Pt–P(2) 98.3(2)°] lies at 67° to the Cu,Pt,W plane. The P–Pt distances differ significantly (Table 3), consequent upon their positions relative to the core atoms. The longer P–Pt distance is associated with the PMe$_3$ ligand transoid to the carbyne-carbon C [P(2)–Pt–C 161.5(5)°]. The weakening of P–Pt bonds *trans* to μ-C atoms has been observed in related structures.[17]

The two CO ligands are non-equivalent. The group C(1)–O(1) semi-bridges the Pt–W bond [W–C(1)–O(1) 162(2)°,

Table 3. Selected internuclear distances (Å) and angles (°) for the compound [CuPtW(μ_3-CC$_6$H$_4$Me-4)(CO)$_2$(PMe$_3$)$_2$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)] (4)

Pt–W	2.779(2)	Cu–W	2.648(3)	Pt–W–Cu	62.2(1)	Pt–W–C	45.9(5)
Cu · · · Pt	2.807(3)	C–Cu	1.96(2)	Cu–W–C	47.3(5)	W–Cu–C	49.6(5)
C–Pt	2.00(2)	C–W	2.03(2)	W–Pt–P(1)	145.3(2)	W–Pt–P(2)	116.1(2)
W–C(1)	1.92(3)	C(1)–O(1)	1.21(4)	P(1)–Pt–P(2)	98.3(2)	W–Pt–C	46.9(5)
W–C(2)	1.97(3)	C(2)–O(2)	1.17(3)			W–Pt–Cu	56.6(1)
Pt–P(1)	2.285(6)	Pt–P(2)	2.341(7)	P(2)–Pt–C	161.5(5)	P(1)–Pt–C	99.6(5)
P(1)–C(11)	1.83(3)	P(2)–C(21)	1.84(3)	W–C–Pt	87.2(7)	Pt–C–C(01)	131.4(13)
P(1)–C(12)	1.79(3)	P(2)–C(22)	1.81(3)	W–C–Cu	83.2(7)	Cu–W–C(1)	120.6(8)
P(1)–C(13)	1.85(3)	P(2)–C(23)	1.82(3)	Pt–C–Cu	90.3(8)	Cu–W–C(2)	74.0(7)
C–C(01)	1.52(3)	C(04)–C(041)	1.57(3)	Pt–W–C(1)	59.5(8)	C–W–C(2)	113.1(9)
Mean C–C (tolyl)	1.38(3)	Mean W–C (cp) [a]	2.42(4)	W–C(1)–O(1)	162(2)	W–C(2)–O(2)	171(3)
Mean Cu–C (cp′) [b]	2.27(3)						

[a] cp = η-C$_5$H$_5$. [b] cp′ = η-C$_5$Me$_5$.

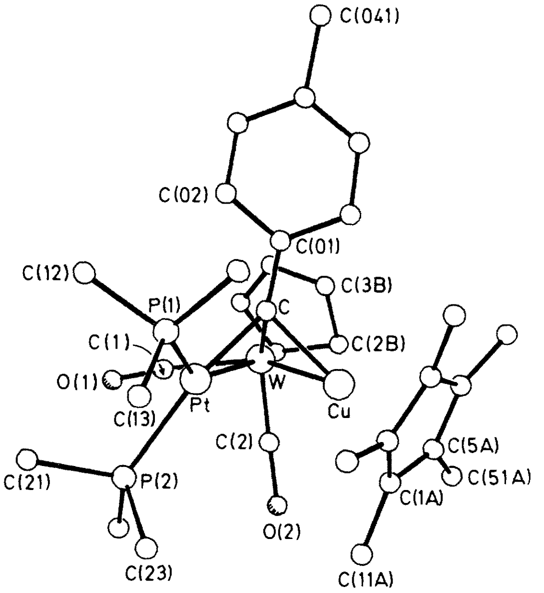

Figure 1. The molecular structure of [CuPtW(μ_3-CC$_6$H$_4$Me-4)(CO)$_2$(PMe$_3$)$_2$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)] (4) showing the crystallographic numbering scheme

Pt–C(1) 2.45 Å], while C(2)–O(2), also non-linear [W–C(2)–O(2) 171(3)°], is considerably further (3.21 Å) from the platinum. The C(1) atom lies almost in the Cu,Pt,W plane, while C(2) is *cis* to the Pt–W vector (83°).

The η-C$_5$H$_5$ ring on the tungsten is positionally disordered (60 : 40), thus the associated parameters are less precise. Both disordered rings incline at *ca.* 70° to the mean plane Cu,Pt,W. The η-C$_5$Me$_5$ ligand exhibits normal geometry, with the Me substituents bending away from the copper atom by *ca.* 0.1 Å from the mean plane of the ring-carbon atoms. The latter plane is inclined at 108° to the Cu,Pt,W plane.

An interesting comparison may be made between the synthesis of (4) and that of the recently reported [18] complex [PtW{μ-C(R)CH$_2$}(CO)$_2$(PMe$_3$)$_2$(η-C$_5$H$_5$)] (R = C$_6$H$_4$Me-4). Both compounds result from the addition of Cu(η-C$_5$Me$_5$) and CH$_2$ groups, respectively, to the C=W bond of the complex [PtW(μ-CR)(CO)$_2$(PMe$_3$)$_2$(η-C$_5$H$_5$)]. Although these two syntheses follow expectations based on isolobal analogies, nevertheless caution is required in placing too much reliance on the predictive power of the model. Thus in contrast with its behaviour towards CH$_2$ or Cu(η-C$_5$Me$_5$), the unsaturated compound [PtW(μ-CR)(CO)$_2$(PMe$_3$)$_2$(η-C$_5$H$_5$)] does not add a Pt(PMe$_3$)$_2$ fragment from [Pt(C$_2$H$_4$)(PMe$_3$)$_2$] to afford [Pt$_2$W(μ_3-CR)(CO)$_2$(PMe$_3$)$_4$(η-C$_5$H$_5$)], a compound which would have a butterfly core structure (CWPt$_2$) akin to (4). Moreover, [Pt$_2$W(μ_3-CR)(CO)$_2$(PMe$_3$)$_4$(η-C$_5$H$_5$)] is not formed by treating [W($\equiv$CR)(CO)$_2$(η-C$_5$Me$_5$)] with excess of [Pt(C$_2$H$_4$)(PMe$_3$)$_2$]. It was mentioned above that the tolylmethylidynetungsten compound readily adds two Cu(η-C$_5$Me$_5$) groups to yield (3). These differences are not unexpected since isolobal mapping between fragments, *e.g.* Cu(η-C$_5$Me$_5$) $\xleftrightarrow[\circ]{}$ Pt(PMe$_3$)$_2$, does not necessarily correlate with the kinetic or thermodynamic stability of products. However, application of the isolobal model [2] as a guideline for synthesis has been remarkably successful, and is further illustrated by the preparation of the compounds (6) and (7), analogues of which are known with an isolobal Pt(cod) (cod = cyclo-octa-1,5-diene) fragment replacing the Cu(η-C$_5$Me$_5$) groups.

Treatment of the unsaturated complex [Pt{W($\equiv$CR)(CO)$_2$(η-C$_5$H$_5$)}$_2$],[19] an analogue of the compounds [Pt(alkyne)$_2$],[20] with excess of [Cu(thf)(η-C$_5$Me$_5$)] gives the red-brown pentanuclear metal complex (6), containing a Cu–W–Pt–W–Cu chain held together by μ_3-CR groups. In a similar synthesis, addition of Pt(cod) groups to [Pt{W($\equiv$CR)(CO)$_2$(η-C$_5$H$_5$)}$_2$] yields [Pt$_3$W$_2$(μ_3-CR)$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$(cod)$_2$] with a Pt–W–Pt–W–Pt chain structure.[21] Compound (6) is unstable in solution, and its i.r. spectrum (Table 1) was, therefore, measured in Nujol. The ^{13}C-{^{1}H} n.m.r. spectrum could be measured at −30 °C (Table 2) and showed a characteristic resonance at δ 272.9 p.p.m., attributable to a μ_3-*C*R group.

We have previously shown [6] that the unsaturated dirhodium compound [Rh$_2$(μ-CO)$_2$(η-C$_5$Me$_5$)$_2$] reacts with [Pt(cod)$_2$] to give [PtRh$_2$(μ-CO)$_2$(η-C$_5$Me$_5$)$_2$(cod)]. The dirhodium species reacts with [Cu(thf)(η-C$_5$Me$_5$)] in a similar manner, to give the deep blue compound (7), the i.r. spectrum of which shows a band due to μ-CO at 1 728 cm^{-1}. The ^{13}C-{^{1}H} spectrum (Table 2) is structurally informative. A triplet signal [*J*(RhC) 44 Hz] at δ 241.5 p.p.m. is characteristic for the μ-CO ligands, and a similar resonance is observed in the spectrum of [PtRh$_2$(μ-CO)$_2$(η-C$_5$Me$_5$)$_2$(cod)] [δ 251.5 p.p.m., triplet, *J*(RhC) 44]. Peaks are also seen in the ^{13}C-{^{1}H} spectrum of (7) corresponding to the presence of Cu(η-C$_5$Me$_5$) and Rh(η-C$_5$Me$_5$) groups in 1 : 2 ratio. The ^{1}H n.m.r. spectrum is in agreement.

It was considered useful to carry out an *X*-ray diffraction study on compound (7). Unfortunately only very small crystals were obtainable. Moreover, the metal atoms proved to be positionally disordered within the metal triangle (Figure 2), and the limited data are summarised in Table 4. Two of the three metal-atom sites are predominantly occupied by Rh atoms (Rh : Cu, 9 : 1) while the remaining site has a correspondingly large contribution from the Cu atom (Ru : Cu,

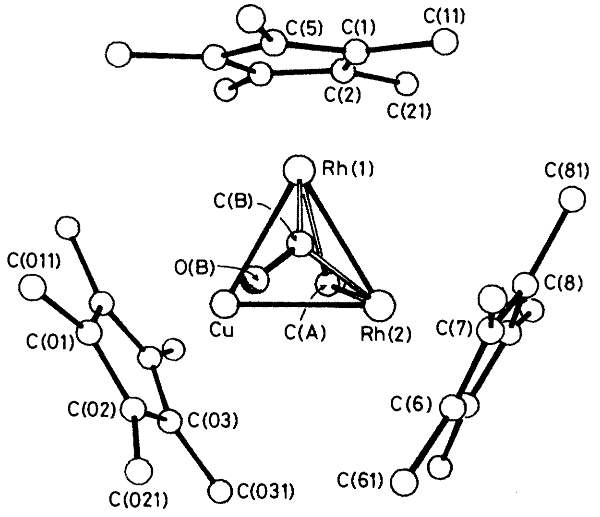

Figure 2. The disordered molecular structure of $[CuRh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_3]$ (7). The atoms are labelled to correspond with the atomic co-ordinates given in Table 6

2 : 8). However, the important feature that all three C_5Me_5 rings adopt an η^5 bonding mode perpendicular to the metal atom triangle is confirmed, *i.e.* the molecule does contain a $Cu(\eta^5\text{-}C_5Me_5)$ fragment. Compound (7) is thus a further example of a species in which a 'carbene-like' metal fragment is bonded to the unsaturated 'ethylene-like' $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$.[12] Other species akin to (7) involve the carbene-like metal fragments PtL_2 [L_2 = cod or $(CO)_2$; L = CO and PPh_3],[6] $Fe(CO)_4$, $Rh(CO)(\eta\text{-}C_5Me_5)$,[22] $Co(CO)(\eta\text{-}C_5Me_5)$,[7] and $M(CO)_5$ (M = Cr, Mo, or W).[6] The CO groups originally bridging the Rh=Rh bonds in $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ are apparently semi-triply bridging in (7) (ν_{CO} 1 728 cm^{-1}), but are ill defined as a result of disorder in the metal triangle. If we consider Rh(1) and Rh(2) as the predominant rhodium sites, then the CO ligands seem to be inclined from 90° towards the predominantly Cu site by 18 and 3°, respectively. Obviously similar tilting can be calculated for all other M_2C permutations. Semi-triply bridging CO ligands are a feature of the structures of $[Rh_3(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2]^-$ (ref. 23) and $[Rh_2Pt(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2]$.[6] As discussed elsewhere,[12] the trirhodium anion corresponds to a situation wherein the carbene-like $Rh(CO)_2^-$ moiety co-ordinates to the as yet unreported species $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ to produce a trimetallacyclopropane structure.

Experimental

Light petroleum refers to that fraction of b.p. 40—60 °C. Experiments were carried out using Schlenk-tube techniques, under a dry oxygen-free nitrogen atmosphere. The n.m.r. measurements were made with JEOL FX 90Q and FX 200 instruments, and i.r. spectra were recorded with a Nicolet MX-1 FT spectrophotometer. The $^{31}P\text{-}\{^1H\}$ n.m.r. chemical shifts are relative to 85% H_3PO_4 (external) and are to high frequency of the standard. The compounds $[W\{=C(OMe)R\}(CO)_5]$,[24] $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$,[25] $[PtW(\mu\text{-}CR)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$,[3] $[Pt\{W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)\}_2]$ [19] (R = C_6H_4Me-4), $[Pt(PhC_2Ph)(PMe_3)_2]$,[20] and $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ [22] were prepared by methods previously described. Analytical data for the new compounds are given in Table 1.

Preparation of the Copper Complexes.—The technique employed involved *in situ* synthesis of the copper reagent at −78 °C followed by addition of the reactant.

Table 4. Mean internuclear separations (Å) within the disordered metal-atom framework M_3 of $[CuRh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_3]$ (7)

M–M	2.56(1)		
M–C(A)	2.03(5)	M–C(B)	2.07(5)
C(A)–O(A)	1.21(5)	C(B)–O(B)	1.41(5)
M–C(I) *	2.19(2)	M–C(II)	2.26(2)
M–C(III)	2.28(2)		

* C(I), C(II), and C(III) refer to rings C(1)–C(5), C(6)–C(10), and C(01)–C(05) (Figure 2 and Table 6). The estimated standard deviations (e.s.d.s) reflect largely the errors in the metal-atom co-ordinates since the $\eta\text{-}C_5Me_5$ rings were refined as rigid groups within which C–C (ring) distances were fixed at 1.42 Å and C–Me distances at 1.54 Å.

(*a*) A mixture of C_5Me_5H (0.40 g, 2.94 mmol) and $LiBu^n$ (2.94 mmol, in hexane solution) in thf (20 cm^3) was cooled to −78 °C. Solid CuCl (0.28 g, 2.8 mmol) was added. After 1 h, the mixture was treated with PPh_3 (0.52 g, 2.0 mmol) and allowed to warm slowly to room temperature. Volatile material was removed *in vacuo* and the residue washed with light petroleum (5 cm^3) and extracted with light petroleum–diethyl ether (1 : 1, 4 × 20 cm^3). The extracts were filtered through a Celite pad (*ca.* 3 cm) and concentrated (*ca.* 20 cm^3) to afford a pale yellow powder. The latter was dissolved in light petroleum–diethyl ether (3 : 1, 40 cm^3) and cooled to −78 °C to give pale yellow *crystals* of $[Cu(PPh_3)(\eta\text{-}C_5Me_5)]$ (1) (0.35 g). This compound is very air sensitive and unstable in solution.

(*b*) The copper reagent was prepared at −78 °C in thf (30 cm^3) using C_5Me_5H (0.43 g, 3.16 mmol), $LiBu^n$ (3.16 mmol), and CuCl (0.34 g, 3.5 mmol). The compound $[W\{=C(OMe)C_6H_4Me\text{-}4\}(CO)_5]$ (0.85 g, 1.85 mmol) was added, and the mixture warmed to room temperature (1 h). Volatile material was removed *in vacuo*. The residue was extracted with light petroleum (5 × 30 cm^3) and the extracts filtered through Celite. Concentration to *ca.* 10 cm^3 and cooling to *ca.* −20 °C afforded magenta crystals of $[CuW\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}(CO)_5(\eta\text{-}C_5Me_5)]$ (2) (0.62 g).

(*c*) Similarly, the compound $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.20 g, 0.50 mmol) was added to $[Cu(thf)(\eta\text{-}C_5Me_5)]$ (1.67 mmol) in thf (20 cm^3) at −78 °C. Removal of volatile material *in vacuo*, extraction with light petroleum (5 × 20 cm^3), and concentration and cooling the extracts to −20 °C afforded dark violet *crystals* of $[Cu_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)_2]$ (3) (0.20 g).

(*d*) The reagent $[Cu(thf)(\eta\text{-}C_5Me_5)]$ (2 mmol) in thf (20 cm^3) was treated with $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ (0.45 g, 0.60 mmol) to give, after work-up in the usual manner, but with extraction of the crude product with diethyl ether, red-black *crystals* of $[CuPtW(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ (4) (0.35 g).

(*e*) Similarly, $[Cu(thf)(\eta\text{-}C_5Me_5)]$ (2 mmol) in thf (20 cm^3) and $[Pt(PhC_2Ph)(PMe_3)_2]$ (0.32 g, 0.61 mmol) gave golden yellow *crystals* of $[CuPt(\mu\text{-}PhC_2Ph)(PMe_3)_2(\eta\text{-}C_5Me_5)]$ (5) (0.20 g).

(*f*) The compound $[Pt\{W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (0.25 g, 0.25 mmol) was added to $[Cu(thf)(\eta\text{-}C_5Me_5)]$ (1 mmol) in thf (15 cm^3) at −78 °C. The mixture was slowly allowed to warm to *ca.* −10 °C. Volatile material was removed *in vacuo*. The oily residue was quickly extracted with light petroleum (7 × 20 cm^3), the extracts filtered through Celite and cooled to −78 °C. The resulting solution at *ca.* −10 °C was concentrated to *ca.* 5 cm^3, and solvent was then decanted from the red-brown solid. The latter was washed with cold pentane (5 × 1 cm^3) and then dried *in vacuo* (2 h) to give red-brown *microcrystals* of $[Cu_2PtW_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2(\eta\text{-}C_5Me_5)_2]$ (6) (0.18 g). The complex begins to decompose in

Table 5. Atomic positional (fractional co-ordinates) with e.s.d.s in parentheses for [$CuPtW(\mu_3-CC_6H_4Me-4)(CO)_2(PMe_3)_2(\eta-C_5H_5)(\eta-C_5Me_5)$] (4)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	0.071 83(9)	0.890 36(5)	0.358 15(4)	C(23)	0.518(3)	1.030(2)	0.276(2)
Pt	0.204 47(9)	0.964 08(5)	0.252 93(4)	C(1A)	0.419(2)	0.767 4(11)	0.303 9(11)
Cu	0.222 9(3)	0.809 71(14)	0.278 86(13)	C(2A)	0.398(3)	0.771 6(12)	0.227 2(11)
P(1)	0.217 4(7)	0.985 6(4)	0.129 5(4)	C(3A)	0.298(3)	0.718 0(12)	0.207 2(13)
P(2)	0.356 4(7)	1.051 3(4)	0.298 4(4)	C(4A)	0.259(3)	0.681 1(12)	0.270 3(12)
C	0.083(2)	0.877 9(11)	0.247 6(10)	C(5A)	0.338(3)	0.712 1(12)	0.332 2(12)
C(01)	−0.020(2)	0.855 2(10)	0.189 1(10)	C(11A)	0.519(3)	0.805 9(13)	0.349 7(13)
C(02)	−0.111(2)	0.909 1(11)	0.157 1(10)	C(21A)	0.476(3)	0.818 3(15)	0.177 5(14)
C(03)	−0.205(3)	0.888 3(12)	0.105 2(11)	C(31A)	0.249(3)	0.694 5(14)	0.127 8(12)
C(04)	−0.214(2)	0.816 1(12)	0.079 9(11)	C(41A)	0.164(3)	0.619 1(13)	0.271 5(14)
C(05)	−0.131(3)	0.764 3(13)	0.108 2(11)	C(51A)	0.332(3)	0.689 8(14)	0.413 2(12)
C(06)	−0.038(2)	0.781 1(11)	0.163 3(10)	C(1B)	−0.043(5)	0.858(3)	0.467 6(15)
C(041)	−0.321(3)	0.792 9(13)	0.019 5(11)	C(2B)	−0.033(5)	0.792(3)	0.424 5(15)
C(1)	0.080(3)	0.998(2)	0.356 8(13)	C(3B)	−0.102(5)	0.804(3)	0.355 2(15)
O(1)	0.067(2)	1.062 7(10)	0.372 7(9)	C(4B)	−0.154(5)	0.878(3)	0.355 5(15)
C(2)	0.240(3)	0.889 3(15)	0.414 3(13)	C(5B)	−0.117(5)	0.911(3)	0.424 9(15)
O(2)	0.330(2)	0.888 6(12)	0.456 2(9)	C(1C)	−0.126(5)	0.830(3)	0.339(2)
C(11)	0.178(3)	0.907 9(12)	0.066 5(12)	C(2C)	−0.037(5)	0.777(3)	0.371(2)
C(12)	0.115(3)	1.060 2(12)	0.096 7(13)	C(3C)	0.014(5)	0.806(3)	0.440(2)
C(13)	0.372(3)	1.014 0(14)	0.095 7(13)	C(4C)	−0.044(5)	0.877(3)	0.451(2)
C(21)	0.331(3)	1.146 0(14)	0.260(2)	C(5C)	−0.131(5)	0.891(3)	0.389(2)
C(22)	0.377(3)	1.0682(15)	0.3970(13)				

Table 6. Atomic positional (fractional co-ordinates) with e.s.d.s in parentheses for [$CuRh_2(\mu-CO)_2(\eta-C_5Me_5)_3$] (7)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh(2)	0.126 9(2)	0.350 4(3)	0.250 00	C(71)	0.329 8(12)	0.320 9(15)	0.312 7(11)
Cu	0.030 8(7)	0.196 5(7)	0.182 4(7)	C(81)	0.201 7(12)	0.481 4(15)	0.413 2(11)
Rh(1)	0.030 7(6)	0.203 5(7)	0.322 3(7)	C(91)	0.081 4(12)	0.637 7(15)	0.303 6(11)
C(1)	0.040 5(12)	0.189(2)	0.439 3(12)	C(101)	0.135 1(12)	0.573 9(15)	0.135 4(11)
C(2)	−0.040 8(12)	0.239(2)	0.428 8(12)	C(01)	0.020 7(15)	0.034(2)	0.107 8(13)
C(3)	−0.088 9(12)	0.151(2)	0.382 0(12)	C(02)	0.066 4(15)	0.122(2)	0.067 1(13)
C(4)	−0.037 3(12)	0.046(2)	0.376 5(12)	C(03)	0.010 7(15)	0.222(2)	0.056 7(13)
C(5)	0.042 7(12)	0.069(2)	0.411 9(12)	C(04)	−0.069 4(15)	0.195(2)	0.091 0(13)
C(11)	0.113 5(12)	0.252(2)	0.481 6(12)	C(05)	−0.063 3(15)	0.079(2)	0.122 6(13)
C(21)	−0.071 5(12)	0.367(2)	0.439 6(12)	C(011)	0.055 9(15)	−0.090(2)	0.131 8(13)
C(31)	−0.180 9(12)	0.166(2)	0.351 3(12)	C(021)	0.159 9(15)	0.122(2)	0.039 2(13)
C(41)	−0.063 4(12)	−0.073(2)	0.338 8(12)	C(031)	0.033 2(15)	0.339(2)	0.015 5(13)
C(51)	0.118 6(12)	−0.019(2)	0.419 3(12)	C(041)	−0.149 0(15)	0.278(2)	0.093 5(13)
C(6)	0.243 0(12)	0.434 3(15)	0.208 3(11)	C(051)	−0.135 0(15)	0.013(2)	0.165 3(13)
C(7)	0.261 1(12)	0.409 2(15)	0.283 8(11)	Cb	0.140(3)	0.183(4)	0.273(3)
C(8)	0.204 9(12)	0.479 7(15)	0.328 0(11)	Ca	0.010(3)	0.351(4)	0.241(4)
C(9)	0.152 0(12)	0.548 4(15)	0.279 8(11)	Oa	−0.055(3)	0.409(3)	0.235(3)
C(10)	0.175 6(12)	0.520 4(15)	0.205 9(11)	Ob	0.196(2)	0.106(3)	0.234(2)
C(61)	0.288 6(12)	0.378 1(15)	0.141 0(11)				

solution after several hours at room temperature, as detected by n.m.r. measurements.

(*g*) The [$Cu(thf)(\eta-C_5Me_5)$] (1.5 mmol) reagent in thf (20 cm^3) was prepared at −78 °C, and [$Rh_2(\mu-CO)_2(\eta-C_5Me_5)_2$] (0.23 g, 0.45 mmol) was added. After warming slowly to room temperature, volatile material was removed *in vacuo* and the residue extracted with light petroleum (8 × 25 cm^3), filtered through a Celite pad, and concentrated *in vacuo* to *ca.* 10 cm^3. Cooling afforded a product contaminated with some [$Rh_2(\mu-CO)_2(\eta-C_5Me_5)_2$]. The latter was readily removed by redissolving in light petroleum (50 cm^3) and bubbling air through the solution which decomposes the dirhodium species without appreciably effecting the desired product. Passage of the mixture through Celite, followed by concentration *in vacuo* and cooling (−20 °C) gave small deep blue *needles* of [$CuRh_2(\mu-CO)_2(\eta-C_5Me_5)_3$] (7) (0.15 g).

Crystal Structure Determination of Complex (4).—Irregular black prisms of compound (4) grown from diethyl ether–light petroleum were found to have limited stability in air and hence were sealed in Lindemann glass capillary tubes under a nitrogen atmosphere. Of the total 2 682 independent reflections measured (ω—2θ scans) at 298 K for $2\theta \leqslant 50°$ on a Nicolet $P2_1m$ four-circle automated diffractometer, 2 238 satisfied the criterion $I \geqslant 1.5\ \sigma(I)$, and only these were used in the solution and refinement of the structure. The intensity data were corrected for Lorentz, polarisation, and absorption effects, the latter by an empirical method based on ψ-scan measurements.

Crystal data. $C_{31}H_{45}CuO_2P_2PtW$, $M = 954.1$, monoclinic, $a = 10.516(5)$, $b = 17.898(8)$, $c = 18.134(6)$ Å, $\beta = 94.25(3)°$, $U = 3\ 403$ Å^3, $Z = 4$, $D_c = 1.87$ g cm^{-3}, $F(000) = 1\ 831$, space group $P2_1/c$ (no. 14), Mo-K_α X-radiation (graphite monochromator), $\lambda = 0.710\ 69$ Å, μ(Mo-K_α) = 83.3 cm^{-1}.

The structure was solved by conventional heavy-atom methods, with all atoms, except Cu, P, Pt, and W, given isotropic thermal parameters. The H atoms were included at their calculated positions ' riding ' on the parent carbon atoms with group isotropic thermal parameters, except for those on the positionally disordered η-C_5H_5 ring, which were not included in the model. Refinement by blocked-cascade least squares converged at R 0.055 (R' 0.046) with weights applied according to the scheme $w = [\sigma^2(F_o) + 0.0005|F_o|^2]^{-1}$ giving a satisfactory weight analysis. Atomic scattering factors were taken from ref. 26, as were the anomalous dispersion corrections and mass absorption coefficients. All computations were carried out on an Eclipse S230 (Data General) computer with the SHELXTL system of programs.[27] Atom co-ordinates for all non-hydrogen atoms are in Table 5.

Crystal Structure Determination of Complex (7).—An exceedingly small black crystal of compound (7) was grown from light petroleum at −78 °C and was sealed in a Lindemann capillary tube under nitrogen. Of the 1 738 reflections ($2\theta \leqslant 40°$; with a ω—2θ scan technique at 298 K), 1 022 satisfied the criterion $I \geqslant 0.5\sigma(I)$, and only these were used in the solution and refinement of the structure. Data were not corrected for *X*-ray absorption effects because the crystal was particularly small and of poor morphology, the linear absorption coefficient was low, and the standard reflections showed a decay of 10% over 56 h exposure. In comparison with the overall low resolution of the data, the residual errors from the lack of absorption correction were considered to be small.

Crystal data. $C_{32}H_{45}CuO_2Rh_2$, $M = 731$, orthorhombic, $a = 15.50(4)$, $b = 11.146(5)$, $c = 18.07(2)$ Å, $U = 3\,122$ Å^3, $Z = 4$, $D_c = 1.56$ g cm^{-3}, $F(000) = 1\,444$, space group $Pca2_1$ (no. 29), $\mu(\text{Mo-}K_\alpha) = 17.3$ cm^{-1}.

The structure was solved as for compound (4), using a model in which the atoms in the metal triangle are positionally disordered between Cu and Rh. Allowing each C_5Me_5 ring complete freedom in the refinement led to an unstable situation consequent on the nature of the disorder. Hence the rings were constrained to regular rigid geometries and refined with isotropic thermal parameters common to groups of either ring or methyl C atoms. Refinement ceased at R 0.095 (R' 0.079). A weighting scheme of the form $w = [\sigma^2(F_o) + 0.0008|F_o|^2]^{-1}$ gave a reasonable weight analysis. Atom coordinates are in Table 6. Computations were as for compound (4).[27]

Acknowledgements

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References

1 Part 23, J. C. Jeffery, K. A. Mead, H. Razay, F. G. A. Stone, M. J. Went, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1984, 1383.

2 R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 711; F. G. A. Stone, *ibid.*, 1984, **23**, 89.

3 T. V. Ashworth, J. A. K. Howard, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1979, 42; *J. Chem. Soc., Dalton Trans.*, 1980, 1609.

4 J. A. Abad, L. W. Bateman, J. C. Jeffery, K. A. Mead, H. Razay, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1983, 2083.

5 (*a*) T. V. Ashworth, J. A. K. Howard, M. Laguna, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 1593; (*b*) J. A. K. Howard, K. A. Mead, J. R. Moss, R. Navarro, F. G. A. Stone, and P. Woodward, *ibid.*, 1981, 743.

6 M. Green, R. M. Mills, G. N. Pain, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 1309; M. Green, J. A. K. Howard, G. N. Pain, and F. G. A. Stone, *ibid.*, p. 1327; R. D. Barr, M. Green, K. Marsden, F. G. A. Stone, and P. Woodward, *ibid.*, 1983, 507.

7 M. Green, D. R. Hankey, J. A. K. Howard, P. Louca, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1983, 757; R. D. Barr, M. Green, J. A. K. Howard, T. B. Marder, and F. G. A. Stone, *ibid.*, p. 759.

8 F. G. A. Stone, in 'Inorganic Chemistry: Toward the 21st Century,' ed. M. H. Chisholm, *ACS Symp. Ser.*, 1983, **211**, 383; *Philos. Trans. R. Soc. London, Ser. A*, 1982, **308**, 87.

9 D. A. Roberts and G. L. Geoffroy, 'Comprehensive Organometallic Chemistry,' eds. E. W. Abel, F. G. A. Stone, and G. Wilkinson, Pergamon Press, 1982, vol. 6, ch. 40.

10 F. A. Cotton and T. J. Marks, *J. Am. Chem. Soc.*, 1969, **91**, 7281; 1970, **92**, 5114.

11 G. A. Carriedo, J. A. K. Howard, and F. G. A. Stone, *J. Organomet. Chem.*, 1983, **250**, C28.

12 A. R. Pinhas, T. A. Albright, P. Hofmann, and R. Hoffmann, *Helv. Chim. Acta*, 1980, **63**, 29.

13 F. A. Cotton and J. Takats, *J. Am. Chem. Soc.*, 1970, **92**, 2353.

14 L. T. J. Delbaere, D. W. McBride, and R. R. Ferguson, *Acta Crystallogr., Sect. B*, 1970, **26**, 515.

15 N. M. Boag, M. Green, J. A. K. Howard, J. L. Spencer, R. F. D. Stansfield, M. D. O. Thomas, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1980, 2182; N. M. Boag, M. Green, J. A. K. Howard, F. G. A. Stone, and H. Wadepohl, *ibid.*, 1981, 862.

16 M. J. Chetcuti, K. Marsden, I. Moore, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 1749.

17 M. J. Chetcuti, J. A. K. Howard, R. M. Mills, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 1757.

18 R. D. Barr, M. Green, J. A. K. Howard, T. B. Marder, I. Moore, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1983, 746.

19 T. V. Ashworth, M. J. Chetcuti, J. A. K. Howard, F. G. A. Stone, S. J. Wisbey, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1981, 763.

20 N. M. Boag, M. Green, D. M. Grove, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 2170.

21 M. R. Awang, G. A. Carriedo, J. A. K. Howard, K. A. Mead, I. Moore, C. M. Nunn, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1983, 964.

22 M. L. Aldridge, M. Green, J. A. K. Howard, G. N. Pain, S. J. Porter, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 1333.

23 W. D. Jones, M. A. White, and R. E. Bergman, *J. Am. Chem. Soc.*, 1978, **100**, 6770.

24 E. O. Fischer, U. Schubert, W. Kleine, and H. Fischer, *Inorg. Synth.*, 1979, **19**, 164.

25 E. O. Fischer, T. L. Lindner, G. Huttner, P. Friedrich, F. R. Kreissl, and J. O. Besenhard, *Chem. Ber.*, 1977, **110**, 3397.

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

27 G. M. Sheldrick, SHELXTL system of crystallographic programs for use with the Nicolet *X*-ray system Cambridge, 1976; updated at Göttingen, 1981.

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