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Synthesis and Characterization of Tungsten–Cobalt, –Rhodium, and –Platinum Compounds and the X-ray Crystal Structures of $RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)$ and $PtW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(O)\}(CO)(PMe_3)(\eta^4\text{-}C_8H_{12})(\eta^5\text{-}C_5H_5)$[†,1]

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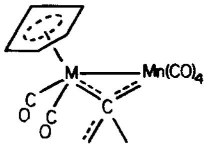
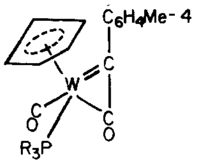
The "ketenyl" tungsten compound $W\{\eta^2\text{-}C(C_6H_4Me\text{-}4)C(O)\}(CO)(PMe_3)(\eta\text{-}C_5H_5)$ reacts with $Co_2(CO)_8$ to give $Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_7(PMe_3)(\eta\text{-}C_5H_5)$, and with $Rh(C_2H_4)_2(\eta^5\text{-}C_9H_7)$ to yield $RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)$. The molecular structure of the latter has been determined by X-ray crystallography (space group D_2^4—$P2_12_12_1$, $a = 9.486$ (2) Å, $b = 15.693$ (6) Å, $c = 16.882$ (5) Å, $Z = 4$). Reactions between bis(cycloocta-1,5-diene)platinum and the compounds $W\{\eta^2\text{-}C(C_6H_4Me\text{-}4)C(O)\}(CO)(PR_3)(\eta\text{-}C_5H_5)$ (PR_3 = PMe_3, PPh_3, $PMe_2(CH_2Ph)$, PMe_2Ph and $PMePh_2$) have been investigated. The nature of the products varies with the tertiary phosphine, but with PMe_3, $PMe_2(CH_2Ph)$, and PMe_2Ph the bimetal complexes $PtW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(O)\}(CO)(PR_3)(\eta\text{-}C_8H_{12})(\eta\text{-}C_5H_5)$ were characterized, and the molecular structure of the trimethylphosphine derivative was established by X-ray crystallography (space group C_{2h}^5—$P2_1/c$, $a = 22.492$ (7) Å, $b = 12.241$ (6) Å, $c = 20.430$ (7) Å, $\beta = 106.07$ (3)°, $Z = 8$). Spectroscopic data (IR and ^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and $^{195}Pt\{^1H\}$ NMR) for all new compounds are reported and discussed.

Introduction

We have previously demonstrated that the compound $W{\equiv}CR(CO)_2(\eta\text{-}C_5H_5)$ ($R = C_6H_4Me\text{-}4$) is a versatile ligand toward low-valent transition-metal complexes, reactions occurring to afford species in which a tolylidyne group bridges bonds between tungsten and other transition elements.[3] Typical of compounds obtained in this manner are $PtW(\mu\text{-}CR)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)$,[4] $Co_2W(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5H_5)$,[5] and $FeRhW(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_5(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)$.[6] These studies, together with the discovery[7,8] of the compounds **1**, prompted us to investigate reactions between the "ketenyl" tungsten complexes **2**[9] and certain low-valent metal compounds. It was expected that the products from **2** would be different in character from those obtained from $W{\equiv}CR(CO)_2(\eta\text{-}C_5H_5)$.



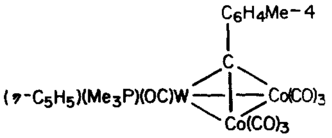
1a, M = Mn
b, M = Re



2a, $PR_3 = PMe_3$
b, $PR_3 = PPh_3$
c, $PR_3 = PMe_2(CH_2Ph)$
d, $PR_3 = PMe_2Ph$
e, $PR_3 = PMePh_2$

Results and Discussion

Treatment of a dichloromethane solution of **2a** with 1 equiv of $Co_2(CO)_8$ at room temperature gave the dark green cluster compound **3**. The ^{13}C NMR spectrum of the latter showed the characteristic resonance for the μ_3-C group at δ 263. The corresponding signal for the triply bridging carbon atom in the spectrum of $Co_2W(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5H_5)$ occurs[5] at δ 257. The ^{31}P NMR spectrum of **3** was informative since the singlet resonance at δ −38.5 showed strong ^{187}W–^{31}P coupling (162 Hz), confirming that the trimethylphosphine ligand was attached to the tungsten atom.



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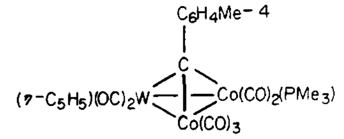
Over a period of ca. 48 h, however, compound **3** isomerizes to **4**, with the PMe_3 group attached to a cobalt atom. This process may be followed by ^{31}P NMR spectroscopy, the peak in the spectrum of **3** at δ −38.5 decreasing in intensity as a new resonance for **4** at δ −4.9 increases in strength. Compound **4** is analogous to the previously described[5] complex $Co_2W(\mu_3\text{-}CR)(CO)_7(PMe_2Ph)(\eta\text{-}C_5H_5)$



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[†] This paper is dedicated to the memory of Professor Rowland Pettit, a friend whose seminal contributions to organometallic chemistry illuminated the field for others to follow.

(1) This paper is part 19 in the series "Chemistry of Di- and Trimetal Complexes with Bridging Carbene or Carbyne Ligands". For part 18 see: Dawkins, G. M.; Green, M.; Mead, K. A.; Salaun, J.-Y.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.*, in press.

(2) Taken in part from the Diploma Theses of C. Sambale and M. F. Schmidt of the Phillips-Universitat, Marburg, German Federal Republic.

(3) For reviews see: Stone, F. G. A. *Acc. Chem. Res.* **1981**, *14*, 318–325; Stone, F. G. A. "Inorganic Chemistry: Towards the 21st Century"; American Chemical Society: Washington, DC, 1982; *ACS Symp. Ser. No. 000*, pp 000–000.

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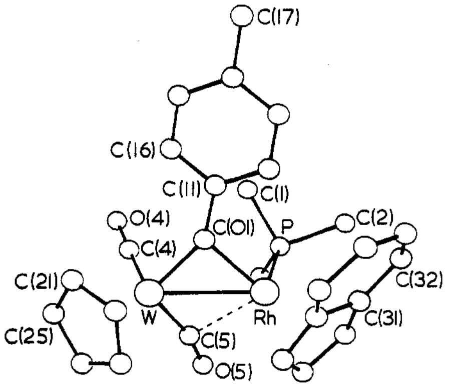
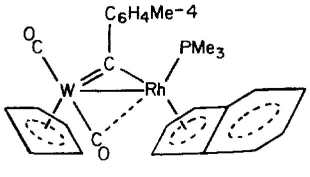


Figure 1. View of the structure of $RhW(\mu\text{-}C_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)$ (**5**) with the atom numbering scheme.

obtained by treating $Co_2W(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5H_5)$ with PMe_2Ph. Like other species of its type, **4** shows more CO stretching bands in its IR spectrum than expected for the existence of a single isomer, a property discussed elsewhere.

The next reaction investigated was that between $Rh(C_2H_4)_2(\eta^5\text{-}C_9H_7)$ and **2a**, in tetrahydrofuran. It was necessary to reflux the mixture for the product to form at an appreciable rate, and in this manner the dimetal compound **5** was isolated in ca. 50% yield. The spectroscopic data for **5** were in accord with the structure illustrated. The ^{13}C NMR spectrum showed the characteristic resonances for the bridging tolylidyne carbon atom at δ 326.6.[3] The one resonance in the ^{31}P NMR spectrum appeared as a doublet at δ 5.04 with $J_{RhC} = 208$ Hz, confirming that the PMe_3 ligand was attached to the rhodium. The IR spectrum of **5** showed two CO stretching bands (1874 and 1775 cm^{-1}), the lower frequency absorption suggesting the presence in the compound of a semibridging or bridging carbonyl ligand.



5

In order to establish the molecular structure of **5**, we carried out a single-crystal X-ray diffraction study. The data in Table I summarise the results of this study, and a view of the molecule is shown in Figure 1.

The Rh–W bond is bridged by the $CC_6H_4Me\text{-}4$ group and semibridged by a CO ligand [W–C(5)–O(5) = 164 (2)°; Rh–C(5) = 2.42 (2) Å]. The tungsten atom has a terminal CO and a cyclopentadienyl group bonded to it, while the rhodium is ligated by PMe_3 and indenyl groups. The $\eta\text{-}C_5H_5$ and $\eta^5\text{-}C_9H_7$ rings are cis to the μ-CRhW plane, in contrast to the cyclopentadienyl and arene ring systems in the complexes $CoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)$[10] and $CrW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_6Me_6)$[11] where a trans configuration is adopted.

In **5**, the μ-C–W separation [1.913 (14) Å] and the angles about C(01) [W–C(01)–C(11) = 146 (1)° and Rh–C(01)–C(11) = 124.2 (9)°] closely resemble those found[10] in $CoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}CMe_5)$ [μ-C–W = 1.913 (7) Å, W–μ-C–C = 142.1 (6)°, and Co–μ-C–C = 124.7 (5)°]. Evidently bonding within the μ-CWM (M = Co or Rh) triangle is very similar in both complexes. Moreover, the μ-C–W separations are intermediate between those found in $W{\equiv}CR(CO)_2(\eta\text{-}C_5H_5)$ [1.82 (2) Å][12] and in $W{=}CPh_2(CO)_5$ [2.14 (2) Å][13] and must reflect considerable multiple-bond character.

Table I. Selected Interatomic Distances (Å) and Interatomic Angles (Deg) with Esd's for $RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)$ (5)

(a) Distances

W–Rh	2.796 (1)	W–C(01)	1.913 (14)
W–C(4)	1.99 (2)	W–C(5)	1.98 (2)
W–C(21)	2.33 (3)	W–C(22)	2.35 (3)
W–C(23)	2.39 (2)	W–C(24)	2.40 (2)
W–C(25)	2.36 (3)	Rh–P	2.247 (5)
Rh–C(01)	2.048 (14)	Rh–C(5)	2.42 (2)
Rh–C(31)	2.48 (2)	Rh–C(36)	2.51 (2)
Rh–C(37)	2.31 (2)	Rh–C(38)	2.21 (2)
Rh–C(39)	2.27 (2)	C(01)–C(11)	1.48 (2)
C(4)–O(4)	1.14 (3)	C(5)–O(5)	1.21 (3)

(b) Angles

Rh–W–C(01)	47.1 (4)	Rh–W–C(4)	102.6 (5)
C(01)–W–C(4)	84.7 (6)	Rh–W–C(5)	57.9 (6)
C(01)–W–C(5)	100.8 (7)	C(4)–W–C(5)	90.0 (7)
W–Rh–P	106.1 (1)	W–Rh–C(01)	43.2 (4)
P–Rh–C(01)	91.6 (4)	W–Rh–C(5)	43.8 (5)
P–Rh–C(5)	93.3 (5)	C(01)–Rh–C(5)	83.8 (6)
W–C(01)–Rh	89.7 (6)	W–C(01)–C(11)	146.0 (10)
Rh–C(01)–C(11)	124.2 (9)	W–C(4)–O(4)	174.3 (14)
W–C(5)–Rh	78.3 (7)	W–C(5)–O(5)	164 (2)
Rh–C(5)–O(5)	116.3 (14)		

The μ-C–Rh distance [2.048 (14) Å] is close to that in $FeRhW(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_5(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)$ [2.035 (6) Å].[6] This suggests that there is little or no μ-C–Rh multiple-bond character, and **5** can thus be regarded as containing a dimetallacyclopropene ring system.[3]

The Rh–W bond [2.796 (1) Å] in **5** may be compared with those found in the di- and trimetal compounds $RhW(\mu\text{-}CRCPhCPh)(CO)_2(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)$ [2.754 (1) Å],[14] $Rh_2W(\mu_3\text{-}CR)(acac)_2(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)$ [2.809 (2) and 2.764 (2) Å],[5] and $FeRhW(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_5(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)$ [2.760 (1) Å].[6] Other features of the molecular structure require no special comment.

Formation of **5** from $Rh(C_2H_4)_2(\eta^5\text{-}C_9H_7)$ and **2a** involves transfer of the PMe_3 group from tungsten to rhodium. However, by following the reaction by IR spectroscopy it was observed that the initial products were the monometallic complexes $W{\equiv}CR(CO)_2(\eta\text{-}C_5H_5)$ and $Rh(CO)(PMe_3)(\eta^5\text{-}C_9H_7)$ which subsequently slowly combined to give **5**. This was confirmed by preparing **5** by treating $W{\equiv}CR(CO)_2(\eta\text{-}C_5H_5)$ with an independently synthesized sample of $Rh(CO)(PMe_3)(\eta^5\text{-}C_9H_7)$.

It was also found that **5** could be obtained by adding PMe_3 to $RhW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)$[11] in dichloromethane solution. When this reaction was monitored by IR and $^{31}P\{^1H\}$ NMR spectroscopy, it was observed that the trimethylphosphine reagent displaces $W{\equiv}CR(CO)_2(\eta\text{-}C_5H_5)$ from the bimetal compound affording $Rh(CO)(PMe_3)(\eta^5\text{-}C_9H_7)$. The latter then combines with the (tolylidyne)tungsten complex to give **5**. This emphasises the isolobal relationship between CR and $W(CO)_2(\eta\text{-}C_5H_5)$ groups, since it is frequently observed that alkyne ligands are more readily replaced by tertiary phosphines than are carbonyl ligands. The displacement of the pseudoalkyne $W{\equiv}CR(CO)_2(\eta\text{-}C_5H_5)$ from $RhW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)$ by PMe_3 is probably aided by an η^5 to η^3 "slippage" of the indenyl group believed to be

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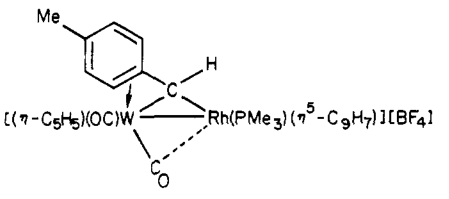
Table II. Selected Interatomic Distances (Å) and Interatomic Angles (Deg) with Esd's for $PtW\{\mu-C_6H_4Me-4)C(O)\}(CO)(PMe_3)(\eta-C_8H_{12})(\eta-C_5H_5)$ (7a)

molecule 1		molecule 2	
	(a) Distances		
W(1)-Pt(1)	2.728 (1)	W(2)-Pt(2)	2.720 (1)
W(1)-P(1)	2.402 (4)	W(2)-P(2)	2.405 (6)
W(1)-C(14)	1.92 (2)	W(2)-C(24)	1.96 (2)
W(1)-C(15)	2.11 (2)	W(2)-C(25)	2.14 (2)
W(1)-C(128)	2.17 (2)	W(2)-C(228)	2.16 (2)
Pt(1)-C(14)	2.273 (15)	Pt(2)-C(24)	2.29 (2)
Pt(1)-C(15)	2.67 (2)	Pt(2)-C(25)	2.703 (15)
Pt(1)-C(128)	2.06 (2)	Pt(2)-C(228)	2.064 (15)
Pt(1)-C(131)	2.21 (2)	Pt(2)-C(231)	2.22 (2)
Pt(1)-C(132)	2.28 (2)	Pt(2)-C(232)	2.19 (2)
Pt(1)-C(135)	2.23 (2)	Pt(2)-C(235)	2.24 (3)
Pt(1)-C(136)	2.23 (3)	Pt(2)-C(236)	2.23 (3)
C(14)-O(14)	1.22 (2)	C(24)-O(24)	1.15 (3)
C(15)-O(15)	1.25 (2)	C(25)-O(25)	1.20 (2)
C(128)-C(15)	1.44 (2)	C(228)-C(25)	1.38 (3)
C(128)-C(121)	1.44 (2)	C(228)-C(221)	1.49 (3)
	(b) Angles		
Pt(1)-W(1)-C(14)	55.3 (5)	Pt(2)-W(2)-C(24)	55.9 (6)
Pt(1)-W(1)-C(15)	65.5 (5)	Pt(2)-W(2)-C(25)	66.3 (4)
C(14)-W(1)-C(15)	112.6 (7)	C(24)-W(2)-C(25)	115.1 (6)
Pt(1)-W(1)-C(128)	48.1 (5)	Pt(2)-W(2)-C(228)	48.4 (4)
C(14)-W(1)-C(128)	102.9 (7)	C(24)-W(2)-C(228)	103.8 (7)
C(15)-W(1)-C(128)	39.4 (5)	C(25)-W(2)-C(228)	37.6 (6)
W(1)-Pt(1)-C(14)	44.0 (5)	W(2)-Pt(2)-C(24)	45.2 (5)
W(1)-Pt(1)-C(128)	51.6 (5)	W(2)-Pt(2)-C(228)	51.5 (4)
W(1)-C(14)-O(14)	158.7 (15)	W(2)-C(24)-O(24)	159.2 (14)
W(1)-C(15)-O(15)	148.8 (12)	W(2)-C(25)-O(25)	146.4 (15)
O(15)-C(15)-C(128)	138.0 (15)	O(25)-C(25)-C(228)	140 (2)
W(1)-C(15)-C(128)	72.4 (9)	W(2)-C(25)-C(228)	71.9 (9)
W(1)-C(128)-Pt(1)	80.3 (6)	W(2)-C(228)-Pt(2)	80.2 (6)
W(1)-C(128)-C(15)	68.2 (9)	W(2)-C(228)-C(25)	70.5 (10)
Pt(1)-C(128)-C(15)	97.7 (11)	Pt(2)-C(228)-C(25)	101.4 (11)
W(1)-C(128)-C(121)	140.9 (13)	W(2)-C(228)-C(221)	136.6 (9)
Pt(1)-C(128)-C(121)	126.5 (11)	Pt(2)-C(228)-C(221)	125.7 (9)
C(15)-C(128)-C(121)	125.1 (13)	C(25)-C(228)-C(221)	125.4 (13)

responsible for the relatively high reactivity of compounds containing $Rh(\eta^5-C_9H_7)$ groups in ligand substitution reactions.[15]

It has been previously shown[16] that the bridged tolylidyne compounds $CoW(\mu-CR)(CO)_3(\eta-C_5H_5)(\eta-C_5Me_5)$ and $PtW(\mu-CR)(CO)_2(PMe_3)_2(\eta-C_5H_5)$ can be readily protonated at the bridging carbon atoms to afford reactive cationic (μ-tolylidene)dimetal complexes. Slow addition of $HBF_4 \cdot Et_2O$ to a saturated solution of **5** in diethyl ether at −20 °C precipitated the salt **6**. The IR spectrum of **6** showed CO stretching bands at 1945 and 1783 cm^{-1}; the latter at a frequency corresponding to that expected for either a semibridging or a bridging carbonyl ligand. The ^{31}P NMR spectrum showed the anticipated doublet resonance for a $RhPMe_3$ group at δ 14.7 [J_{RhP} = 173 Hz]. The ^1H NMR spectrum had a resonance [doublet, J_{PH} = 20 Hz] at δ 7.95 which is characteristic for the CH proton of the μ-CHR group.[16] The salt **6** is a relatively unstable species in solution, and this property made it impossible to obtain high-quality ^{13}C NMR data. The postulated $\mu-\eta^1,\eta^3$ interaction of the $CH(C_6H_4Me-4)$ group with the dimetal system in **6** is by analogy with that established by X-ray crystallography for this system in $[PtW\{\mu-\eta^1,\eta^3-CH(C_6H_4Me-4)\}(CO)_2(PMe_3)_2(\eta-C_5H_5)][BF_4]$[16] and for the $C(C_6H_4Me-4)_2$ group in $Mo_2\{\mu-\eta^1,\eta^3-C(C_6H_4Me-4)_2\}(CO)_4(\eta-C_5H_5)_2$.[17]



6

As part of our studies on the synthesis of compounds with bonds between tungsten and other metals, we have investigated the reaction of **2a** with $Pt(\eta-C_8H_{12})_2$ (C_8H_{12} = cycloocta-1,5-diene). Previously we have shown[18] that $Pt(C_2H_4)_3$ reacts with $W{\equiv}CR(CO)_2(\eta-C_5H_5)$ to give the trimetal compound $PtW_2(\mu-CC_6H_4Me-4)_2(CO)_4(\eta-C_5H_5)_2$. However, reaction of $W{\equiv}CR(CO)_2(\eta-C_5H_5)$ with $Pt(\eta-C_8H_{12})_2$ failed to yield isolable products. Nevertheless, it was thought that the ketenyl tungsten compound might be a more favorable reagent for the platinum species. This was because $Pt(\eta-C_8H_{12})_2$ is known[19] to form a stable product with diphenylcyclopropenone, and the latter is closely related to **2a** through the isolobal mapping between the fragments CR and $W(CO)(PMe_3)(\eta-C_5H_5)$.

Addition of $Pt(\eta-C_8H_{12})_2$ to **2a** in tetrahydrofuran at 0 °C gave an orange crystalline compound **7a**. The spectroscopic properties of the latter did not unambiguously define the molecular structure, and hence a single-crystal

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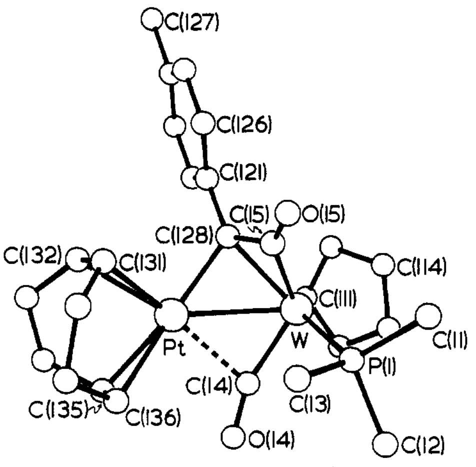
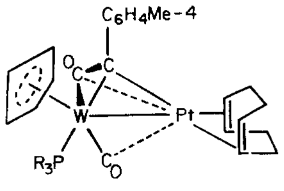


Figure 2. View of the structure of $PtW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(O)\}(CO)(PMe_3)(\eta^4\text{-}C_8H_{12})(\eta\text{-}C_5H_5)$ (**7a**) with the atom numbering scheme.

X-ray diffraction study was carried out. There proved to be two independent molecules in the asymmetric unit of **7a**, with very similar geometries. One of these is shown in Figure 2, with the atom numbering scheme. Table II lists selected inter-atomic distances and angles for both molecules, and in the following discussion reference is made to the parameters of molecule (1).



7a, $PR_3 = PMe_3$
b, $PR_3 = PMe_2(CH_2Ph)$
c, $PR_3 = PMe_2Ph$

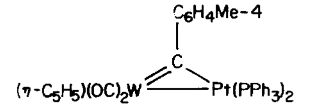
Compound **7a** can be regarded as a complex in which a $Pt(\eta\text{-}C_8H_{12})$ fragment is coordinated by **2a**. The μ-C(128)–W(1) bond is bridged by a carbonyl group [W(1)–C(15)–O(15) = 149 (1)° and C(128)–C(15)–O(15) = 138 (2)°]. The remaining CO group semibridges the Pt–W bond [Pt(1)–C(14) = 2.27 (2) Å and W(1)–C(14)–O(14) = 159 (2)°]. The IR spectrum of **7a** is not entirely consistent with this result, suggesting a somewhat different structure in solution. The spectrum shows two strong CO absorptions at 1689 and 1625 cm^{-1}, one of which can be ascribed to C(15)–O(15). However, C(14)–O(14) should give rise to a band in the IR in the 1850–1750-cm^{-1} region, suggesting that perhaps in **7a**, and its analogues described below, the semibridging CO ligand becomes fully bridging in solution.

The relatively short Pt(1)–C(15) distance [2.67 (2) Å] in **7a** suggests a tendency toward η^3-bonding of the **2a** fragment to the platinum atom, reflected in the ^{13}C NMR spectrum by ^{195}Pt–$^{13}C(15)$ coupling (44 Hz). A similar bonding mode of diphenylcyclopropenone to platinum may occur in the relatively unstable isolobal complex $Pt\{\eta^3\text{-}PhC{:}C(Ph)C(O)\}(PPh_3)_2$.[20] It is interesting to compare the synthesis of **7a** with the reaction of bis(cycloocta-1,5-diene)platinum with diphenylcyclopropenone, which affords a diplatinum compound through breakage of the C=C bond in the ketone.[19] In the reaction between **2a** and $Pt(C_8H_{12})_2$ the corresponding bond, C(128)–W(1), is preserved.

Not unexpectedly, in **7a** the μ-C(128)–W [2.17 (2) Å], W–C(15) [2.11 (2) Å], and C(15)–C(128) [1.44 (2) Å] separations are all significantly longer than the corresponding distances in the parent molecule **2a**, these being 1.97, 2.07, and 1.32 Å, respectively.[9] The dimensions of the Pt(1)-W(1)C(128) ring in **7a** are typical of those found in structurally related molecules. Thus Pt(1)–W(1) [2.728 (1)], Pt(1)–C(128) [2.06 (2)] and W(1)–C(128) [2.17 (2) Å] compare with corresponding distances of 2.795 (1), 2.053 (14), and 2.166 (14) Å found[16] in $[PtW\{\mu\text{-}\eta^1,\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)][BF_4]$.

The platinum atom in **7a** adopts an approximately square-planar geometry with the ligated double bonds of the cod ligand being essentially transoid to the Pt–W and Pt–C(128) bonds, respectively. The dimensions of the cod group and the separations of the atoms C(131), C(132), C(136), and C(135) from the platinum are similar to those established in a variety of other complexes containing a $Pt(\eta\text{-}C_8H_{12})$ fragment.[21]

Compound **2b** was also prepared by Kreissl et al.,[9] and we have investigated its reaction with $Pt(\eta\text{-}C_8H_{12})_2$. Surprisingly, the previously reported[22] bimetal compound **8** was the only product, isolated from what was evidently a complicated process. Possibly **2b** reverts to $W{\equiv}CR(CO)_2(\eta\text{-}C_5H_5)$ and PPh_3. The latter would displace cycloocta-1,5-diene from platinum, perhaps affording $Pt(PPh_3)_2$ in situ, which would add readily to the (tolylidyne)tungsten compound yielding **8**.[4] The unexpected product from **2b** and $Pt(\eta\text{-}C_8H_{12})_2$ prompted a more exhaustive study of reactions of the platinum reagent with ketenyltungsten complexes, leading to synthesis of the precursors **2c–e**.



$$(\eta\text{-}C_5H_5)(OC)_2W\overset{\overset{\displaystyle C_6H_4Me\text{-}4}{|}}{\overset{C}{\diagup\;\diagdown}}Pt(PPh_3)_2$$

8

The benzyldimethylphosphine derivative **2c** gave the bimetal complex **7b**. The spectroscopic properties of the latter were similar to those of **7a**, indicating similar structures for the two products. Thus in its IR spectrum **7b** had CO bands at 1691 and 1624 cm^{-1}. The ^{31}P NMR spectrum showed a singlet resonance at δ 9.3 with ^{187}W and ^{195}Pt satellite peaks [J_{WP} = 337, J_{PtP} = 52 Hz] commensurate with the presence of the WPR_3 group. The corresponding data for **7a** are δ −1.38 [s, J_{WP} = 337, J_{PtP} = 54 Hz]. The ^{13}C NMR spectrum of **7b** showed all the resonances expected for the structure proposed. Noteworthy are doublet signals for the semibridging CO ligand at δ 246.5 [J_{PC} = 10, J_{PtC} = 146 Hz] and W(μ-CO)C group at δ 235 [J_{PC} = 23, J_{PtC} = 39 Hz]. The ^{195}Pt satellites observed on the latter signal are in accord with the incipient η^3-bonding mode for the W(μ-CO)C ring to platinum, discussed above for **7a**. In the spectrum of **7b**, the four chemically inequivalent ligating carbon atoms of the cycloocta-1,5-diene ligand (δ 111.7, 102.5, 98.3, and 86.6) all show ^{195}Pt–^{13}C coupling. The values of the coupling constants suggest that the signals at δ 111.7 and 102.5 [J_{PtC}(av) = 142 Hz] are due to the C=C group transoid to the Pt–W

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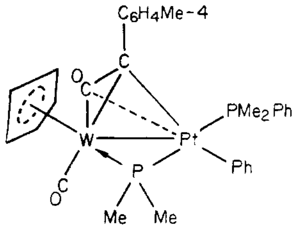
bond, while the peaks at δ 98.3 and 86.6 [J_{PtC}(av) = 113 Hz] are due to the C═C group transoid to the carbon atom bridging the metal–metal bond. The ^{195}Pt NMR spectra of **7a** [δ 153.6 (d, J_{PPt} = 51 Hz)] and **7b** [δ 139.0 (d, J_{PPt} = 50 Hz)] are very similar.

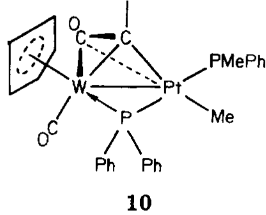
Whereas **2a** and **2c** gave analogous products in their reactions with Pt(η-C_8H_{12})$_2$, the compound **2d** reacted with bis(cycloocta-1,5-diene)platinum to give a mixture of two complexes. One of these, **7c** was characterized (see Experimental Section) as being structurally similar to **7a,b**. The identity of the other product **9** has not been firmly established but is tentatively assigned the structure shown, on the basis of its NMR spectra, although its instability and insolubility in solution inhibited measurement of a good quality ^{13}C spectrum.

The ^{31}P NMR spectrum of **9** showed two resonances, both doublets with ^{195}Pt satellite peaks. One peak had a chemical shift (δ −15.5) and coupling constants (J_{PP} = 219 and J_{PtP} = 3056 Hz) diagnostic for a trans P·Pt·P group.[23-25] The chemical shift of the other resonance (δ 118 (J_{PP} = 219, J_{PtP} = 1406, J_{WP} = 222 Hz) provides strong evidence for the presence in **9** of a μ-PR_2 ligand, since signals for such groups in three-membered dimetalla rings are shifted markedly downfield from those of tertiary phosphines. The observation of both ^{195}Pt and ^{187}W couplings on the signal at δ 118 further supports the assignment. As mentioned above, some difficulties were encountered in measuring the ^{13}C NMR spectrum, and it was not possible to observe a resonance for the carbon atom bridging the metal–metal bond. However, signals characteristic of the two CO groups were observed, together with peaks attributable to Ph (two environments), C_6H_4Me-4, PMe, and C_5H_5 groups.



9

The reaction between Pt(η-C_8H_{12})$_2$ and **2e** gave as the only product a complex **10**, the structure of which is tentatively assigned on the basis of spectroscopic data (Experimental Section), as done for **9** above. We are unable to account for the formation of **9** and **10** in these reactions, which obviously involve C–P bond cleavage and transfer of tertiary phosphine groups from tungsten to platinum. However, reactions of zero-valent platinum compounds with cleavage of P–Ph bonds and formation of μ-PPh_2 and Pt–Ph linkages have been previously observed.[26]



10

During attempts to grow crystals of **7a,b** for X-ray diffraction studies, it was observed that in solution at 25 °C these complexes decomposed (ca. 24 h), yielding W≡CR(CO)$_2$(η-C_5H_5) and the compounds PtW(μ-CC_6H_4Me-4)(CO)$_2$(PR_3)$_2$(η-C_5H_5) [PR_3 = PMe_3 or $PMe_2(CH_2Ph)$].[4,22] It was also observed that PMe_3 reacts with **7a** to displace the cycloocta-1,5-diene ligand and afford PtW{μ-C(C_6H_4Me-4)C(O)}(CO)(PMe_3)$_3$(η-C_5H_5), **11**.

Experimental Section

General Remarks. Infrared spectra were recorded in CH_2Cl_2 on a Nicolet MX-1 FT spectrometer. NMR spectra (^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, and ^{195}Pt{^{1}H}) were measured on a JEOL FX 90Q Fourier transform spectrometer. Chemical shifts δ (ppm) are to high frequency, with ^{31}P relative to 85% H_3PO_4 (external) and ^{195}Pt relative to $\Xi_{^{195}Pt}$ = 21.4 MHz. Unless specified to the contrary, NMR spectra were measured in $CDCl_3$.

All solvents were freshly distilled prior to use, and reactions were carried out under nitrogen by using Schlenk tube techniques. Chromatography was carried out on alumina (Brockman, activity II). Microanalyses were determined at the School of Chemistry, University of Bristol. The compounds Pt(η-C_8H_{12})$_2$,[27] Rh(C_2H_4)$_2$(η-C_9H_7),[15] W≡CC_6H_4Me-4(CO)$_2$(η-C_5H_5),[12] and W{η^2-C(C_6H_4Me-4)CO}(CO)(PR_3)(η-C_5H_5) (PR_3 = PMe_3 or PPh_3)[9] were synthesized by literature procedures. However, certain new mononuclear rhodium and tungsten complexes were prepared as precursors for the work described herein:

Rh(CO)(PMe$_3$)(η^5-C$_9$H$_7$) was obtained by bubbling CO gas through a hexane (10 mL) solution of Rh(C_2H_4)$_2$(η^5-C_9H_7) (0.14 g, 0.50 mmol) to generate Rh(CO)$_2$(η^5-C_9H_7) in situ. Trimethylphosphine (0.50 mmol) was added to the mixture cooled to −20 °C. After being warmed to room temperature, the solution was stirred (1 h). Removal of solvent in vacuo afforded a residue which was dissolved in hexane–dichloromethane (4:1) and chromatographed to afford, after removal of solvent, yellow crystals (70 mg, 43%): IR ν_{CO} 1943 (vs) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 1.38 (d of d, 9 H, MeP, J_{PH} = 9, J_{RhH} = 1 Hz), 5.30 (d, 2 H, C_9H_7, J_{HH} = 2 Hz), 5.97 (d of d, 1 H, C_9H_7, J_{HH} = 2, J_{RhH} = 2 Hz), 6.7–7.2 (m, 4 H, C_9H_7); ^{31}P NMR (CD_2Cl_2–CH_2Cl_2) δ −2.53 (d, J_{RhP} = 190 Hz). Anal. Calcd for $C_{13}H_{16}OPRh$: C, 48.4; H, 5.0. Found: C, 47.8; H. 4.6.

W{η^2-C(C$_6$H$_4$Me-4)C(O)}(CO)(PR$_3$)(η-C$_5$H$_5$) (2). The compound W≡CC_6H_4Me-4(CO)$_2$(η-C_5H_5) (0.41 g, 1.00 mmol) in CH_2Cl_2 (25 mL) was treated with $PMe_2(CH_2Ph)$ (1.00 mmol) and the mixture stirred at 25 °C (3 h). Solvent was removed in vacuo and the residue dissolved in CH_2Cl_2 (5 mL) and chromatographed. Elution with the same solvent afforded, after evaporation, brick-red **2c** (0.49 g, 88%): IR ν_{CO} 1889 (vs), 1681 (s) cm^{-1}; ^{1}H NMR δ 1.33 (d, 3 H, MeP, J_{PH} = 10 Hz), 1.53 (d, 3 H, MeP, J_{PH} = 10 Hz), 2.32 (s, 3 H, Me-4), 2.88 (d, 1 H, CH_2, J_{PH} = 10), 3.02 (d, 1 H, CH_2, J_{PH} = 10 Hz), 5.46 (s, 5 H, C_5H_5), 6.8 −7.9 (m, 9 H, C_6H_4, Ph); ^{31}P NMR δ −2.1 (J_{WP} = 410 Hz). Anal. Calcd for $C_{24}H_{25}O_2PW$: C, 51.5; H, 4.4. Found: C, 51.5; H, 4.4.

A similar synthesis afforded compound **2d** (0.51 g, 93%): IR ν_{CO} 1889 (vs), 1691 (s) cm^{-1}; ^{1}H NMR δ 1.3 (d, 3 H, MeP, J_{WP} = 10 Hz), 1.9 (d, 3 H, MeP, J_{WP} = 10 Hz), 2.3 (s, 3 H, Me-4), 5.4 (s, 5 H, C_5H_5), 7.0–7.7 (m, 9 H, C_6H_4, Ph); ^{31}P NMR δ 7.0 (J_{WP} = 411 Hz). Anal. Calcd for $C_{25}H_{23}O_2PW$: C, 50.6; H, 4.2. Found: C, 49.9; H. 4.1.

Similarly, for **2e** (0.54 g, 89%): IR ν_{CO} 1889 (vs), 1693 (s) cm^{-1}; ^{1}H NMR δ 2.14 (d, 3 H, MeP, J_{PH} = 9 Hz), 2.29 (s, 3 H, Me-4), 5.39 (s, 5 H, C_5H_5), 7.2–7.7 (m, 14 H, C_6H_4, Ph); ^{31}P NMR δ 19.1 (J_{WP} = 417 Hz).

Reaction of 2a with Co$_2$(CO)$_8$. A CH_2Cl_2 (10 mL) solution of **2a** (0.36 g, 0.76 mmol) was treated with $Co_2(CO)_8$ (0.26 g, 0.76 mmol) and the mixture stirred for 1 h. Solvent was removed in vacuo and the green residue chromatographed using CH_2Cl_2–hexane (2:5). Removal of solvent and recrystallization gave dark green crystals **Co$_2$W(μ_3-CC$_6$H$_4$Me-4)(CO)$_7$(PMe$_3$)(η-C$_5$H$_5$) (3)**

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(24) In ref 23, ^{31}P chemical shifts are quoted to low frequency of the standard (85% H_3PO_4, external), in contrast to the more recent convention employed herein and in ref 22.

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(27) Spencer, J. L. *Inorg. Synth.* **1979**, *19*, 213–215.

Table III. Crystallographic Details for 5 and 7a

	$C_{27}H_{28}O_2PRhW$, 5	$C_{26}H_{33}O_2PPtW \cdot {}^1/_2CH_2Cl_2$, 7a
fw	702.2	829.9
space group	D_2^4–$P2_12_12_1$	C_{2h}^5–$P2_1/c$
a, Å	9.486 (2)	22.492 (7)
b, Å	15.693 (6)	12.241 (6)
c, Å	16.882 (5)	20.430 (7)
β, deg		106.07 (3)
V, Å^3	2513 (1)	5404 (4)
Z	4	8
ρ(calcd), g cm^{-3}	1.86	2.04
temp, °C	22	22
cryst dimens, mm	0.10 × 0.10 × 0.50	0.35 × 0.35 × 0.36
radiatn	graphite monochromator, Mo Kα ($\bar{\lambda}$ = 0.710 69 Å)	graphite monochromator, Mo Kα ($\bar{\lambda}$ = 0.710 69 Å)
diffractometer	Nicolet $P3m$	Nicolet $P3m$
abs coeff, cm^{-1}	μ(Mo Kα) = 54.0	μ(Mo Kα) = 95.0
scan range, deg	$3.0 \leqslant 2\theta \leqslant 50$	$3.0 \leqslant 2\theta \leqslant 50$
scan technique	θ–2θ	θ–2θ
data collected	h,k,l	$h,k,\pm l$
total unique data	2649	7189
unique data with $F_o \geqslant \sigma(F_o)$	2119 (n = 5)	5577 (n = 6)

(0.48 g, 85%): mp 189–190 °C; IR ν_{CO} 2047 (s), 2003 (vs), 1982 (s), 1964 (s), 1900 (m) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 1.26 (d, 9 H, MeP, J_{PH} = 10 Hz), 2.24 (s, 3 H, Me-4), 5.08 (s, 5 H, C_5H_5), 6.8–7.2 (m, 4 H, C_6H_4); ^{31}P NMR (CD_2Cl_2–CH_2Cl_2) δ –38.5 (s, J_{WP} = 162 Hz); ^{13}C NMR (CD_2Cl_2–CH_2Cl_2) δ 263 (μ_3-C), 207 (CO), 161 (C^1-(C_6H_4Me-4)), 134, 127 (C_6H_4), 91 (C_5H_5), 20.0 (Me-4), 19.0 (d, MeP, J_{PC} = 15 Hz). Anal. Calcd for $C_{23}H_{21}Co_2O_7PW$: C, 37.3; H, 2.9. Found: C, 37.2; H, 3.0.

A CH_2Cl_2 solution of **3** after three days at room temperature isomerized to **4**: mp 125–128 °C; IR ν_{CO} 2054 (m), 2041 (m), 2002 (vs), 1983 (sh), 1979 (s), 1962 (sh), 1908 (w), 1849 (w), 1833 (w) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 1.37 (d, 9 H, MeP, J_{PH} = 9 Hz), 2.31 (s, 3 H, Me-4), 5.16 (s, 5 H, C_5H_5), 6.93–7.41 (m, 4 H, C_6H_4); ^{31}P NMR (CD_2Cl_2–CH_2Cl_2) δ –4.9. Anal. Calcd for $C_{23}H_{21}Co_2O_7PW$: C, 37.3; H, 2.9. Found: C, 36.8; H, 2.6.

Reaction of 2a with $Rh(C_2H_4)_2(\eta^5\text{-}C_9H_7)$. A sample of **2a** (0.39 g, 0.81 mmol) was added to $Rh(C_2H_4)_2(\eta^5\text{-}C_9H_7)$ (0.22 g, 0.81 mmol) in tetrahydrofuran (20 mL). The mixture was refluxed (12 h), solvent removed in vacuo, and the residue chromatographed with CH_2Cl_2–hexane (1:4) to obtain black crystals of **$RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\mu\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)$ (5)** (0.29 g, 52%): mp 183 °C; IR ν_{CO} 1874 (vs), 1775 (m) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 1.06 (d of d, 9 H, MeP, J_{PH} = 9, J_{RhH} = 2 Hz), 2.31 (s, 3 H, Me-4), 5.50 (s, 5 H, C_5H_5), 5.84 (s, 2 H, C_9H_7), 5.92 (s, 1 H, C_9H_7), 6.42–7.36 (m, 8 H, C_6H_4, C_9H_7); ^{31}P NMR (CD_2Cl_2–CH_2Cl_2) δ 5.04 (d, J_{RhP} = 208 Hz); ^{13}C NMR (CD_2Cl_2–CH_2Cl_2) δ 326.6 (d, μ-C, J_{RhC} = 22 Hz), 238.1 (d, μ-CO, J_{RhC} = 31 Hz), 216.8 (CO), 154.7 (C^1-(C_6H_4Me-4)), 136.7–104.9 (C_6H_4, C_9H_7), 91.7 (C_5H_5), 87.3, 80.2, 77.0 (C_9H_7), 21.9 (Me-4), 18.8 (d, MeP, J_{PC} = 30 Hz). Anal. Calcd for $C_{27}H_{28}O_2PRhW$: C, 46.2; H, 4.0. Found: C, 46.4; H, 4.0.

Compound **5** was also prepared by treating Rh(CO)(PMe_3)(η^5-C_9H_7) with $W{\equiv}CC_6H_4Me\text{-}4(CO)_2(\eta\text{-}C_5H_5)$ in CH_2Cl_2 at room temperature (24 h) and by reacting $RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)$ with PMe_3 in CH_2Cl_2 at room temperature (3 h). These reactions were monitored by IR and NMR spectroscopy (see Discussion).

Protonation of 5. A sample of **5** (0.13 g, 0.18 mmol) in Et_2O (20 mL) was treated with $HBF_4{\cdot}Et_2O$ (0.2 mL) at 0 °C leading to immediate precipitation of the ocre salt **$[RhW\{\mu\text{-}\eta^1,\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PMe_3)(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)][BF_4]$ (6)**: mp 97–98 °C dec; IR ν_{CO} 1946 (vs), 1783 (s) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 1.67 (d of d, 9 H, MeP, J_{PH} = 11, J_{RhH} = 1 Hz), 2.37 (s, 3 H, Me-4), 4.61 (s, 5 H, C_5H_5), 5.46 (s, 1 H, C_9H_7), 5.81 (s, 1 H, C_9H_7), 6.02 (s, 1 H, C_9H_7), 7.07–7.17 (m, 4 H, C_9H_7), 7.28–7.44 (m, 4 H, C_6H_4), 7.95 (d, 1 H, μ-CH, J_{PH} = 20 Hz); ^{31}P NMR (CD_2Cl_2) δ 14.7 (d, J_{RhP} = 173 Hz); ^{13}C NMR (CD_2Cl_2–CH_2Cl_2) δ 225.4 (μ-CO), 134–128 (C_6H_4), 126.5–96.3 (C_9H_7), 92.8 (C_5H_5), 90.5, 84.0 (C_9H_7), 21.5 (Me-4), 16.8 (d, MeP, J_{PC} = 34 Hz). Anal. Calcd for $C_{27}H_{29}BF_4O_2PRhW$: C, 41.0; H, 3.7. Found: C, 39.7; H, 4.0.

Reactions of the Compounds 2 with $Pt(\eta\text{-}C_8H_{12})_2$. A solution of **2a** (0.33 g, 0.69 mmol) in tetrahydrofuran (20 mL) at 0 °C was treated with $Pt(\eta\text{-}C_8H_{12})_2$ (0.28 g, 0.69 mmol), and the mixture was stirred and warmed to room temperature (3 h). Solvent was removed in vacuo and the residue chromatographed with CH_2Cl_2 to give orange crystals of **$PtW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(O)\}(CO)(PMe_3)(\eta\text{-}C_8H_{12})(\eta\text{-}C_5H_5)$ (7a)** (0.28 g, 51%): mp 111–113 °C; IR ν_{CO} 1689 (vs), 1625 (vs) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 1.49 (d, 9 H, MeP, J_{PH} = 10 Hz), 2.3 (m, br, 11 H, Me-4, $CH_2(C_8H_{12})$), 4.94 (m, 4 H, CH), 5.30 (s, 5 H, C_5H_5), 7.05–7.30 (m, 4 H, C_6H_4); ^{31}P NMR (CD_2Cl_2) δ –1.38 (J_{WP} = 337, J_{PtP} = 54 Hz); ^{195}Pt NMR (CD_2Cl_2) δ 153.6 (d, J_{PPt} = 54 Hz); ^{13}C NMR (CD_2Cl_2–CH_2Cl_2) δ 244.5 (d, PtWCO, J_{PC} = 12, J_{PtC} = 240 Hz), 231.8 (d, CO, J_{PC} = 22, J_{PtC} = 44 Hz), 221.4 (μ-C), 140.9 (C^1(C_6H_4Me-4)), 133.7, 126.5 (C_6H_4), 110.6 (CH(C_8H_{12}), J_{PtC} = 149 Hz), 101.6 (CH(C_8H_{12}), J_{PtC} = 132 Hz), 96.4 (CH(C_8H_{12}), J_{PtC} = 117 Hz), 89.8 (C_5H_5), 85.2 (CH(C_8H_{12}), J_{PtC} = 110 Hz), 30.6, 29.7, 29.0, 28.6 ($CH_2(C_8H_{12})$), 20.3 (Me-4), 19.9 (d, MeP, J_{PC} = 24 Hz). Anal. Calcd for $C_{26}H_{33}O_2PPtW$: C, 39.6; H, 4.2. Found: C, 39.0; H, 4.3.

Similarly **2c** (0.28 g, 0.50 mmol) and $Pt(\eta\text{-}C_8H_{12})_2$ (0.20 g, 0.50 mmol) gave, after chromatography (hexane–CH_2Cl_2, 1:1), **$PtW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(O)\}(CO)\{PMe_2(CH_2Ph)\}(\eta\text{-}C_8H_{12})(\eta\text{-}C_5H_5)$ (7b)** (0.26 g, 60%): mp 110–123 °C dec; IR ν_{CO} 1691 (vs), 1624 (vs) cm^{-1}; ^{1}H NMR δ 1.33 (d, 3 H, MeP, J_{PH} = 9 Hz), 1.39 (d, 3 H, MeP, J_{PH} = 9 Hz), 2.20 (m, br, 8 H, $CH_2(C_8H_{12})$), 2.31 (s, 3 H, Me-4), 3.27 (d of d, 2 H, CH_2, J_{PH} = 10, J_{HH} = 9 Hz), 4.90–4.92 (m, 9 H, CH(C_8H_{12}), C_5H_5), 7.26 (m, 9 H, C_6H_4, Ph); ^{31}P NMR δ 9.3 (J_{PtP} = 51, J_{WP} = 337 Hz); ^{195}Pt NMR δ 139 (d, J_{PPt} = 51 Hz); ^{13}C NMR δ 246.5 (d, PtWCO, J_{PC} = 10, J_{PtC} = 146 Hz), 234.5 (d, CO, J_{PC} = 23, J_{PtC} = 39 Hz), 140.8 (C^1(C_6H_4Me-4)), 136.2–128.2 (C_6H_4, Ph), 111.7 (CH(C_8H_{12}), J_{PtC} = 152 Hz), 102.5 (CH(C_8H_{12}), J_{PtC} = 132 Hz), 98.3 (CH(C_8H_{12}), J_{PtC} = 117 Hz), 90.6 (C_5H_5), 86.6 (CH(C_8H_{12}), J_{PtC} = 109 Hz), 41.0 (d, CH_2P, J_{PC} = 25 Hz), 31.0, 30.2, 29.8, 29.4 ($CH_2(C_8H_{12})$), 21.1 (Me-4), 18.2 (d, MeP, J_{PC} = 30 Hz), 17.0 (d, MeP, J_{PC} = 30 Hz). Anal. Calcd for $C_{33}H_{37}O_2PtW$: C, 44.5; H, 4.3. Found: C, 43.2; H, 4.6.

The product mixture from **2d** (0.27 g, 0.50 mmol) and $Pt(\eta\text{-}C_8H_{12})_2$ (0.20 g, 0.50 mmol) was chromatographed. Elution of the column with hexane–CH_2Cl_2 gave brown **$PtW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(O)\}(\mu\text{-}PMe_2)(Ph)(CO)(PMe_2Ph)(\eta\text{-}C_5H_5)$ (9)** (0.11 g, 26%): IR ν_{CO} 1873 (s), 1732 (m), cm^{-1}; ^{1}H NMR δ 1.3–1.5 (m, 12 H, μ-MeP), 2.30 (s, 3 H, Me-4), 5.04 (s, 5 H, C_5H_5), 6.5–7.4 (m, 14 H, C_6H_4), Ph); ^{31}P NMR δ –15.5 (d, PMe_2Ph, J_{PP} = 219, J_{PtP} = 3056 Hz), 118.2 (d, μ-P, J_{PP} = 219, J_{PtP} = 1406, J_{WP} = 222 Hz); ^{13}C NMR δ 223.6 (d, WCO, J_{PC} = 7 Hz), 207.8 (CO, J_{PtC} = 29 Hz), 147.5–122.2 (C_6H_4, Ph), 91.2 (C_5H_5), 25.9 (d, MeP, J_{PC} = 31, J_{PtC} = 32 Hz), 22.2 (d, MeP, J_{PC} = 36, J_{PtC} = 22 Hz), 21.0 (Me-4), 15.0 (d, MeP, J_{PC} = 36, J_{PtC} = 42 Hz), 12.6 (d, MeP, J_{PC} = 34, J_{PtC} = 34 Hz). Anal. Calcd for $C_{31}H_{34}O_2P_2PtW$: C, 42.3; H, 3.8. Found: C, 43.3; H, 4.4. Elution of the chromatography column with CH_2Cl_2 afforded orange **$PtW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(O)\}(CO)(PMe_2Ph)(\eta\text{-}C_8H_{12})(\eta\text{-}C_5H_5)$ (7c)** (0.26 g, 49%): mp 125 °C; IR ν_{CO} 1685 (vs), 1622 (vs) cm^{-1}; ^{1}H NMR δ 1.70 (d, 3 H, MeP, J_{PH} = 10 Hz), 2.15 (d, 3 H, MeP, J_{PH} = 10 Hz), 2.30 (m, 11 H, Me-4, $CH_2(C_8H_{12})$), 4.81 (m, 4 H, CH(C_8H_{12})), 5.28 (s, 5 H, C_5H_5), 6.8–7.8 (m, 9 H, C_6H_4, Ph); ^{31}P NMR δ 5.4 (J_{PPt} = 58, J_{WP} = 336 Hz); ^{195}Pt NMR δ 151.0 (d, J_{PPt} = 58 Hz). Anal. Calcd for

Table IV. Positional Parameters (and Esd's) for $RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)$

atom	*x*	*y*	*z*
W	0.36765 (7)	0.15872 (4)	0.29942 (4)
Rh	0.09159 (12)	0.10627 (8)	0.26795 (7)
P	0.1042 (6)	0.0220 (4)	0.1605 (3)
C(1)	0.238 (3)	−0.061 (2)	0.1529 (14)
C(2)	−0.048 (3)	−0.047 (3)	0.145 (2)
C(3)	0.113 (7)	0.076 (3)	0.0705 (12)
C(01)	0.2704 (15)	0.0532 (10)	0.3148 (7)
C(11)	0.2789 (11)	−0.0350 (5)	0.3462 (6)
C(12)	0.1584 (11)	−0.0796 (5)	0.3692 (6)
C(13)	0.1703 (11)	−0.1620 (5)	0.3994 (6)
C(14)	0.3027 (11)	−0.1999 (5)	0.4065 (6)
C(15)	0.4232 (11)	−0.1554 (5)	0.3835 (6)
C(16)	0.4113 (11)	−0.0729 (5)	0.3533 (6)
C(17)	0.316 (3)	−0.2884 (13)	0.4443 (12)
C(21)	0.522 (3)	0.1713 (12)	0.4063 (14)
C(22)	0.386 (3)	0.1963 (12)	0.4338 (14)
C(23)	0.348 (3)	0.2722 (12)	0.3936 (14)
C(24)	0.459 (3)	0.2943 (12)	0.3413 (14)
C(25)	0.567 (3)	0.2319 (12)	0.3492 (14)
C(31)	−0.145 (2)	0.0801 (12)	0.3258 (9)
C(32)	−0.212 (2)	0.0017 (13)	0.3398 (12)
C(33)	−0.200 (3)	−0.031 (2)	0.4124 (14)
C(34)	−0.130 (3)	0.0086 (14)	0.4742 (10)
C(35)	−0.058 (3)	0.085 (2)	0.4625 (11)
C(36)	−0.063 (2)	0.1230 (12)	0.3877 (10)
C(37)	−0.008 (3)	0.2007 (12)	0.3566 (12)
C(38)	−0.065 (3)	0.2103 (13)	0.2790 (11)
C(39)	−0.141 (2)	0.1401 (12)	0.2568 (13)
O(4)	0.545 (2)	0.0529 (10)	0.1786 (8)
C(5)	0.254 (3)	0.2100 (14)	0.2138 (12)
O(5)	0.2070 (15)	0.2570 (10)	0.1634 (8)

$C_{32}H_{35}O_2PPtW$: C, 42.5; H, 4.1. Found: C, 41.1; H, 4.2.

Reaction of **2e** (0.30 g, 0.50 mmol) with $Pt(\eta\text{-}C_8H_{12})_2$ (0.20 g, 0.50 mmol) in tetrahydrofuran (20 mL) gave brown-orange **$PtW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(O)\}(\mu\text{-}PPh_2)(Me)(CO)(PMePh_2)(\eta\text{-}C_5H_5)$ (10)** (0.23 g, 47%): IR ν_{CO} 1877 (vs), 1734 (s) cm^{-1}; ^1H NMR δ 1.26 (s, 3 H, MePt, J_{PtH} = 646 Hz), 2.32 (d, 3 H, MeP, J_{PH} = 8 Hz), 2.36 (s, 3 H, Me-4), 5.28 (s, 5 H, C_5H_5), 6.9–7.4 (m, 24 H, C_6H_4, Ph); ^{31}P NMR δ −1.1 (d, $PMePh_2$, J_{PP} = 224, J_{PtP} = 3212 Hz), 132.6 (d, μ-PPh_2, J_{PP} = 223, J_{PtP} = 1538, J_{WP} = 348 Hz).

Decomposition of 7b in CH_2Cl_2. A sample of **7b** (0.43 g, 0.50 mmol) in CH_2Cl_2 (25 mL) was stirred for 24 h at 25 °C. Solvent was removed in vacuo and the residue chromatographed with hexane–CH_2Cl_2 (1:1) and subsequently with CH_2Cl_2 to give **$PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2\{PMe_2(CH_2Ph)\}_2(\eta\text{-}C_5H_5)$** (0.20 g, 43%): IR ν_{CO} 1895 (vs), 1803 (s) cm^{-1}; ^1H NMR δ 1.00 (d, 6 H, MeP, J_{PH} = 8 Hz), 1.32 (d, 6 H, MeP, J_{PH} = 8 Hz), 2.34 (s, 3 H, Me-4), 2.75 (d, 4 H, CH_2, J_{PH} = 10 Hz), 5.29 (s, 5 H, C_5H_5), 6.6–7.2 (m, 14 H, C_6H_4, Ph); ^{31}P NMR δ −2.9 (J_{PtP} = 4087 Hz), −13.5 (J_{PtP} = 2771 Hz).

Reaction of 7a with PMe_3. A solution of **7a** (0.22 g, 0.30 mmol) in CH_2Cl_2 (20 mL) was treated with PMe_3 (0.6 mmol). Solvent was removed in vacuo and the residue chromatographed by using hexane–CH_2Cl_2 (1:1) to elute trace products and tetrahydrofuran to give red crystals of **$PtW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(O)\}(CO)(PMe_3)_3(\eta\text{-}C_5H_5)$ (11)** (0.17 g, 71%): IR ν_{CO} 1705 (vs), 1641 (s) cm^{-1}; ^1H NMR δ 1.35 (d, 9 H, MeP, J_{PH} = 9 Hz), 1.53 (d, 9 H, MeP, J_{PH} = 8 Hz), 1.67 (d, 9 H, MeP, J_{PH} = 8 Hz), 2.30 (s, 3 H, Me-4), 4.80 (s, 5 H, C_5H_5), 7.0–7.3 (m, 4 H, C_6H_4); ^{31}P NMR δ 0.2 (d, PW, J_{PP} = 7, J_{WP} = 313, J_{PtP} = 17 Hz), −12.9 (d, PPt, J_{PP} = 12, J_{PtP} = 3390 Hz), −30.0 (d of d, PPt, J_{PP} = 12, 7, J_{PtP} = 3427 Hz). Anal. Calcd for $C_{24}H_{39}O_2P_3PtW$: C, 34.6; H, 4.6. Found: C, 34.1; H, 4.5.

Crystal Structure Determinations. (a) $RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)$. A deep red crystal of **5** was grown from hexane–CH_2Cl_2. Details concerning crystal characteristics and X-ray diffraction methodology are shown in Table III. Intensity data were collected and corrected for Lorentz, polarization, and absorption effeccts, as previously described.[5,28]

Table V. Positional Parameters (and Esd's) for $PtW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(O)\}(CO)(PMe_3)(\eta\text{-}C_8H_{12})(\eta\text{-}C_5H_5)\cdot{}^1/_2CH_2Cl_2$

atom	*x*	*y*	*z*
W(1)	0.35891 (3)	0.82708 (5)	0.38537 (3)
Pt(1)	0.44772 (3)	0.89530 (5)	0.32685 (3)
W(2)	0.08662 (3)	0.30213 (6)	0.36319 (3)
Pt(2)	0.15624 (3)	0.36345 (5)	0.48904 (3)
P(1)	0.2940 (3)	0.7247 (4)	0.2924 (3)
P(2)	0.1606 (3)	0.1904 (5)	0.3289 (3)
C(11)	0.2102 (10)	0.753 (2)	0.2697 (12)
C(12)	0.2968 (10)	0.5739 (15)	0.3017 (13)
C(13)	0.3128 (10)	0.739 (2)	0.2091 (10)
C(14)	0.4222 (8)	0.7352 (12)	0.3685 (8)
O(14)	0.4549 (6)	0.6545 (9)	0.3712 (7)
C(15)	0.3296 (8)	0.9494 (13)	0.3104 (9)
O(15)	0.2885 (6)	0.9861 (10)	0.2605 (6)
C(111)	0.3915 (6)	0.8317 (15)	0.5061 (8)
C(112)	0.3699 (6)	0.7243 (15)	0.4865 (8)
C(113)	0.3059 (6)	0.7307 (15)	0.4520 (8)
C(114)	0.2879 (6)	0.8421 (15)	0.4502 (8)
C(115)	0.3408 (6)	0.9045 (15)	0.4837 (8)
C(121)	0.3943 (5)	1.0980 (7)	0.3856 (6)
C(122)	0.4340 (5)	1.1158 (7)	0.4505 (6)
C(123)	0.4427 (5)	1.2214 (7)	0.4772 (6)
C(124)	0.4118 (5)	1.3092 (7)	0.4389 (6)
C(125)	0.3722 (5)	1.2913 (7)	0.3740 (6)
C(126)	0.3635 (5)	1.1857 (7)	0.3474 (6)
C(127)	0.4218 (11)	1.4256 (2)	0.4698 (12)
C(128)	0.3850 (7)	0.9884 (14)	0.3591 (9)
C(138)	0.4567 (11)	0.965 (2)	0.1865 (11)
C(137)	0.4951 (12)	0.861 (2)	0.1954 (13)
C(136)	0.4947 (9)	0.796 (2)	0.2644 (10)
C(135)	0.5371 (9)	0.8140 (15)	0.3291 (12)
C(134)	0.5877 (11)	0.900 (2)	0.342 (2)
C(133)	0.5670 (11)	1.013 (2)	0.3150 (11)
C(132)	0.5028 (10)	1.0414 (13)	0.3064 (10)
C(131)	0.4531 (9)	1.0192 (13)	0.2503 (9)
C(21)	0.1336 (12)	0.056 (3)	0.2976 (13)
C(22)	0.1952 (10)	0.252 (3)	0.2668 (12)
C(23)	0.2326 (11)	0.149 (2)	0.3955 (11)
C(24)	0.1512 (10)	0.4150 (14)	0.3797 (10)
O(24)	0.1797 (7)	0.4879 (11)	0.3692 (7)
C(25)	0.1028 (8)	0.1731 (13)	0.4368 (9)
O(25)	0.1128 (7)	0.0771 (11)	0.4474 (8)
C(211)	0.0053 (11)	0.428 (2)	0.3154 (14)
C(212)	0.0381 (11)	0.410 (2)	0.2662 (14)
C(213)	0.0313 (11)	0.298 (2)	0.2472 (14)
C(214)	−0.0057 (11)	0.247 (2)	0.2848 (14)
C(215)	−0.0217 (11)	0.328 (2)	0.3269 (14)
C(221)	0.0299 (5)	0.2584 (9)	0.4990 (6)
C(222)	−0.0037 (5)	0.3522 (9)	0.5043 (6)
C(223)	−0.0495 (5)	0.3481 (9)	0.5385 (6)
C(224)	−0.0616 (5)	0.2503 (9)	0.5674 (6)
C(225)	−0.0279 (5)	0.1566 (9)	0.5622 (6)
C(226)	0.0178 (5)	0.1606 (9)	0.5280 (6)
C(227)	−0.1097 (10)	0.243 (2)	0.6085 (12)
C(228)	0.0799 (8)	0.2623 (11)	0.4638 (8)
C(231)	0.1903 (10)	0.302 (2)	0.5952 (9)
C(232)	0.1503 (10)	0.389 (2)	0.5930 (10)
C(233)	0.1723 (12)	0.508 (2)	0.6169 (13)
C(234)	0.218 (2)	0.555 (3)	0.5831 (15)
C(235)	0.2204 (10)	0.506 (2)	0.5194 (10)
C(236)	0.2553 (11)	0.414 (2)	0.5129 (10)
C(237)	0.2956 (12)	0.339 (3)	0.5639 (14)
C(238)	0.2597 (10)	0.312 (2)	0.6208 (11)
C	0.1605 (11)	0.573 (4)	0.066 (2)
CL(1)	0.2373 (5)	0.5024 (10)	0.0911 (7)
CL(2)	0.1349 (6)	0.5296 (13)	0.1414 (6)

The structure was solved and all non-hydrogen atoms were located by conventional heavy-atom and difference Fourier methods. Hydrogen atoms were not included in the refinement. The cyclopentadienyl ring was treated as a rigid group (C–C = 1.420 Å) but not the indenyl ligand. Refinement by blocked cascade least squares, with anisotropic temperature factors for all non-hydrogen atoms, led to R = 0.047 (R' = 0.047) with a weighting scheme of the form $w = [\sigma^2(F_o) + 0.001|F_o|^2]^{-1}$. The

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[28] Sheldrick, G. M. SHELXTL programs for use with the Nicolet *P3m X*-ray system.

final electron density difference synthesis showed no peaks >1 e Å^{-3}. Scattering factors were used and anomalous dispersion corrections were applied to all non-hydrogen atoms.[29] All computations were carried out on an "Eclipse" (Data General) minicomputer with the "SHELXTL" system of programs.[28] Atomic coordinates are given in Table IV.

(b) $PtW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(O)\}(CO)(PMe_3)(\eta\text{-}C_8H_{12})(\eta\text{-}C_5H_5)\cdot{}^1/_2CH_2Cl_2$. A well-formed red parallelepiped crystal of **7a** was obtained from a CH_2Cl_2–hexane solution. Details are given in Table III, and the solution and refinement of the structure were as described for **5**, but with the cyclopentadienyl and aryl rings treated as rigid groups (C–C(C_5H_5) = 1.420 Å and C–C(C_6H_4) = 1.395 Å). Refinement converged at R = 0.048 (R' = 0.051) with a weighting scheme of the form $w = [\sigma^2(F_o) + 0.001|F_o|]^{-1}$. The final electron-density difference synthesis showed no peaks >1.4 e Å^{-3}. Atomic coordinates are listed in Table V.

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[29] "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1962; Vol. III, pp 201–13.

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Registry No. 2a, 61202-59-3; **2c**, 83114-97-0; **2d**, 83114-98-1; **2e**, 83114-99-2; **3**, 83115-00-8; **4**, 83115-01-9; **5**, 83134-38-7; **6**, 83115-03-1; **7a**, 83115-04-2; **7b**, 83115-05-3; **7c**, 83115-07-5; **9**, 83115-06-4; **10**, 83115-08-6; **11**, 83115-10-0; $Rh(CO)(PMe_3)(\eta^5\text{-}C_9H_7)$, 83114-96-9; $PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2\{PMe_2(CH_2Ph)\}_2(\eta\text{-}C_5H_5)$, 83115-09-7; $Rh(C_2H_4)_2(\eta^5\text{-}C_9H_7)$, 63428-46-6; $W{\equiv}CC_6H_4Me\text{-}4\text{-}(CO)_2(\eta\text{-}C_5H_5)$, 60260-15-3; $Pt(\eta\text{-}C_8H_{12})_2$, 12130-66-4; $Co_2(CO)_8$, 10210-68-1; Co, 7440-48-4; W, 7440-33-7; Rh, 7440-16-6; Pt, 7440-06-4.

Supplementary Material Available: Observed and calculated structure factor tables for compounds **5** and **7a** as well as tables of anisotropic thermal parameters and a full list of bond lengths (59 pages). Ordering information is given on any current masthead page.

(Pentamethylcyclopentadienyl)rhodium and -iridium Complexes. 37.[1] Synthesis and X-ray Structure Determination of Bis(μ_3-methylidyne)tris[(η^5-pentamethylcyclopentadienyl)rhodium][†]

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Under appropriate conditions reaction of $[(C_5Me_5Rh)_2Cl_4]$ with Al_2Me_6 gives bis(μ_3-methylidyne)tris[(η^5-pentamethylcyclopentadienyl)rhodium], $[(C_5Me_5Rh)_3(CH)_2]$, **4**, in 50% yield rather than *trans*-$[(C_5Me_5Rh)_2(\mu\text{-}CH_2)_2(CH_3)_2]$. The stoichiometry of formation is formally represented by the equation $3[(C_5Me_5Rh)_2Cl_4] + 2Al_2Me_6 = 2[(C_5Me_5Rh)_3(CH)_2] + 2Al_2Cl_6 + 8CH_4$. Complex **4** was characterized spectroscopically and by an X-ray structure determination [rhombohedral, a = 11.918 (7) Å, α = 101.91 (4)°, Z = 2, and space group $R\bar{3}$ (C_{3i}^2, No. 148); 1441 reflections with $I > 3\sigma(I)$; R = 0.027]. This showed an equilateral triangle of rhodiums each η^5 bonded to a C_5Me_5 and capped top and bottom by a μ_3-CH ligand. From its dimensions the Rh_3C_2 skeleton appears to be very tightly bound; this may account for the high thermal stability of **4**.

We have recently described the syntheses of the *cis*- and *trans*-dimethylbis(μ-methylene)dirhodium complexes **2a** and **2b** from reaction of $[(C_5Me_5Rh)_2Cl_4]$ (**1**) and Al_2Me_6 (or LiMe) in hydrocarbon solvents.[2,3] Recent studies of the mechanism by which **2** were formed showed that the kinetically controlled product was the cis-isomer **2a** which isomerized, in the presence of a Lewis acid, into the thermodynamically more stable trans-isomer **2b**. The cis-complex **2a** was, in turn, obtained from an intermediate, identified by low-temperature ^{13}C NMR spectroscopy as $C_5Me_5RhMe_2MeAlMe_xCl_{2-x}$, **3**, by careful oxidation or addition of a hydrogen acceptor such as acetone.[3,4] Under different conditions, however, the trinuclear bis(μ_3-methylidyne) complex **4** is formed in this reaction (Scheme I).

Results and Discussion

Structure of 4. Complex **4** crystallized from chloroform in orange needles and was air stable in both solid and solution. It was readily soluble in hydrocarbons, dichloromethane, and ether but less so in acetone or methanol. Elemental analysis and the mass spectrum gave the formula $C_{32}H_{47}Rh_3$ (the molecular ion at m/e 740 was also the parent ion). The ^1H NMR spectrum showed the presence of a singlet at δ 1.88 and a quartet at δ 13.18 (J = 5.5 Hz), with relative intensity ratio close to 45:2. The very low-field chemical shift of the latter resonance suggested the presence of a methylidyne ligand; for example, in $[(CpRh)_3(\mu_3\text{-}CH)(\mu\text{-}CO)_2]BF_4$ the μ_3-CH resonates at δ 16.28,[5] while in $[Co_3(\mu_3\text{-}CH)(CO)_9]$ it is at δ 12.08.[6] The multiplicity of the signal indicated that it was coupled, and

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[†] To Rowland Pettit, a brilliant and dedicated chemist, whom we remember with affection.

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