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Synthesis of tungsten–rhodium complexes with bridging alkylidyne groups

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Abstract

Treatment of the alkylidyne-tungsten compounds $[W(\equiv CR)(CO)_2L]$ (R = Me or C_6H_4Me-4, L = η-C_5H_5 or $HB(pz)_3$ = hydrotris(pyrazol-1-yl)borate) with the salt $[Rh(PPh_3)_2(cod)][PF_6]$ (cod = cyclo-octa-1,5-diene) affords the dimetal complexes $[WRh(\mu\text{-}CR)(CO)_2(PPh_3)_2L][PF_6]$. The species $[WRh(\mu\text{-}CMe)(CO)_2(cod)\{HB(pz)_3\}][BF_4]$ has been prepared by treating $[W(\equiv CMe)(CO)_2\{HB(pz)_3\}]$ with $[Rh(thf)_2(cod)][BF_4]$ (thf = tetrahydrofuran), generated in situ from $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$. The reaction between $[Rh(NCMe)_3(\eta\text{-}C_5Me_5)][PF_6]_2$ and $[W(\equiv CMe)(CO)_2\{HB(pz)_3\}]$ affords the salt $[WRh(\mu\text{-}CMe)(\mu\text{-}CO)(CO)(\eta\text{-}C_5Me_5)\{HB(pz)_3\}][PF_6]_2$. Some reactions of the species $[WRh(\mu\text{-}CR)(CO)_2(PPh_3)_2L][PF_6]$ are reported.

Introduction

Addition of low-valent metal–ligand fragments to the compounds $[W(\equiv CR)(CO)_2L]$ (R = alkyl or aryl, L = η-C_5H_5, η-C_5Me_5, or $HB(pz)_3$ {hydrotris(pyrazol-1-yl)borate}) affords a wide range of complexes in which tungsten atoms are linked to one or other of the transition elements. In these products the heteronuclear metal–metal bonds are spanned by alkylidyne groups [1,2]. Complexes with tungsten–rhodium bonds prepared in this manner include: $[WRh(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)L]$ (I, R = C_6H_4Me-4, L = acac (acetylacetonate), η^5-C_9H_7 (indenyl), or η-C_5Me_5; R = Me, L = η^5-C_9H_7 or η-C_5Me_5), $[WRh_2(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)L_2]$ (II, R = C_6H_4Me-4, L = acac or η^5-C_9H_7; R = Me, L = η-C_5Me_5) [3,4], $[WRh(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_9H_7)\{HB(pz)_3\}]$ (III), $[WRh_2(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_2(\eta^5\text{-}C_9H_7)_2\{HB(pz)_3\}]$ (IV, R = Me or C_6H_4Me-4) [5], $[WRh(\mu\text{-}CR)(CO)_3(\eta^5\text{-}C_9H_7)(\eta\text{-}C_5Me_5)]$ (V, R = Me or C_6H_4Me-4), and $[WRh_2(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5Me_5)_3]$ (VI) [6,7*]. In this paper we describe the synthesis and some reactions of a series of dimetal tungsten–rhodium salts. These have been

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* Reference number with asterisk indicates a note in the list of references.

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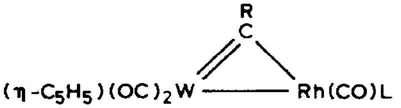
obtained by treating reagents of the type [W(≡CR)(CO)$_2$L] with rhodium salts containing labile ligands which are readily displaced by the more powerful ligating properties of C≡W groups. Reactions of alkylidyne-tungsten compounds with cationic metal–ligand fragments have as yet been little studied [8].

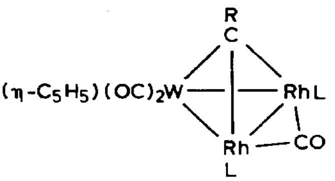
Results and discussion

Addition of solid [Rh(PPh$_3$)$_2$(cod)][PF$_6$] (cod = cyclo-octa-1,5-diene) to CH_2Cl_2 solutions of [W(≡CR)(CO)$_2$(η-C_5H_5)] at room temperature affords the complexes [WRh(μ-CR)(CO)$_2$(PPh$_3$)$_2$(η-C_5H_5)][PF$_6$] (R = C_6H_4Me-4 (VIIa) or Me (VIIb)). The related compounds [WRh(μ-CR)(CO)$_2$(PPh$_3$)$_2${HB(pz)$_3$}][PF$_6$] (VIIc and VIId) may be obtained by refluxing in toluene mixtures of [W(≡CR)(CO)$_2${HB(pz)$_3$}] and [Rh(PPh$_3$)$_2$(cod)][PF$_6$]. Compound VIIc may also be prepared by mixing the reactants in CH_2Cl_2 at room temperature, but under these conditions product formation takes several hours, and yields are lower. The complex [WRh(μ-CMe)(CO)$_2$(cod){HB(pz)$_3$}][BF$_4$] (VIII) was obtained from [W(≡CMe)(CO)$_2${HB(pz)$_3$}] and [Rh(thf)$_2$(cod)][BF$_4$] (thf = tetrahydrofuran). The latter was generated in situ by treating [Rh$_2$(μ-Cl)$_2$(cod)$_2$] with AgBF$_4$.

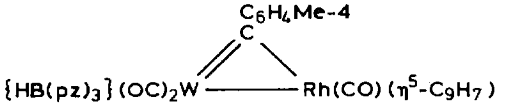
Data for the compounds VII and VIII are given in Tables 1 and 2, and are in agreement with the formulations proposed. In the IR, each compound shows two bands in the CO stretching region; the absorption at ca. 1800 cm^{-1} strongly



	R	L
Ia	C_6H_4Me-4	acac
Ib	C_6H_4Me-4	η^5-C_9H_7
Ic	C_6H_4Me-4	η-C_5Me_5
Id	Me	η^5-C_9H_7
Ie	Me	η-C_5Me_5



	R	L
IIa	C_6H_4Me-4	acac
IIb	C_6H_4Me-4	η^5-C_9H_7
IIc	Me	η-C_5Me_5



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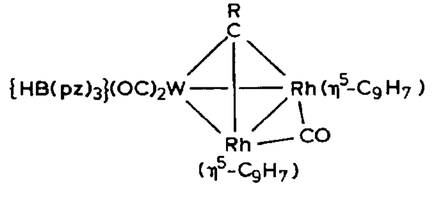
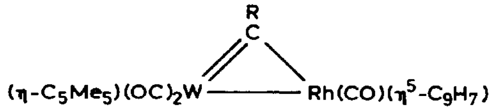
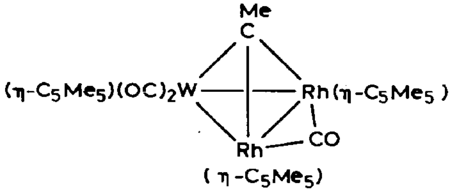


	R
IVa	Me
IVb	C_6H_4Me-4



	R
Va	Me
Vb	C_6H_4Me-4



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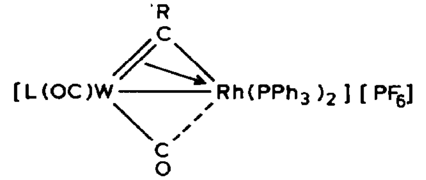
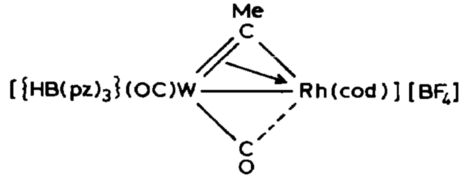


	R	L
VIIa	C_6H_4Me-4	η-C_5H_5
VIIb	Me	η-C_5H_5
VIIc	C_6H_4Me-4	$HB(pz)_3$
VIId	Me	$HB(pz)_3$



(VIII)

suggesting that one of the carbonyl groups semi-bridges the W–Rh bond. The NMR data (Table 2) are informative. Unfortunately, measurements could not be made at low temperatures due to the insolubility of the compounds. This feature is also responsible for the non-detection of the ^{13}C $\{^1H\}$ NMR peak due to the μ-C nucleus in VIIc. However, characteristic signals for the bridging alkylidyne-carbon group are clearly seen in the spectra of VIIa (356.8), VIIb (362.0), VIId (346.1) and VIII (338.2 ppm). Moreover, ^{103}Rh–^{13}C coupling was observed on the μ-C signals of VIId and VIII. The observed chemical shifts are relatively deshielded, and may be compared with the corresponding signals in the ^{13}C $\{^1H\}$ NMR spectra of the dimetal compounds Ia (310.0) [3], Ib (312.4), Id (323.4) [4a], and III (296.6 ppm) [5]. For reasons discussed in detail elsewhere [9], the somewhat greater deshielding of the alkylidyne-carbon nuclei in the spectra of the compounds VII and VIII may indicate that in these species the C≡W fragments are formally acting as four-electron donors to the rhodium centres. Indeed, this feature would allow rhodium to attain a 16-electron rather than a 14-electron valence shell in the cations.

The compounds VII and VIII evidently undergo dynamic behaviour in solution. In the ^{31}P $\{^1H\}$ NMR spectra (Table 2) only one resonance is observed for the chemically non-equivalent PPh_3 groups in VII, which must be *cis* and *trans* to the μ-C groups. Moreover, in the ^{13}C $\{^1H\}$ NMR spectra only one CO signal is observed. The appearance of this resonance as a doublet, due to ^{103}Rh–^{13}C coupling, is in agreement, however, with the IR spectra in indicating a semi-bridging carbonyl ligand. As mentioned above, limiting spectra at low temperatures could not be recorded due to the insolubility of the complexes. We have discussed earlier

(*Continued on p. 120*)

Table 1

Analytical and other data for the tungsten–rhodium compounds

Compound	Colour	Yield (%)	$\nu_{max}(CO)$ [a] (cm^{-1})		Analysis (Found (calc) (%))		
					C	H	N
$[WRh(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (VIIa)	Black	90	1988s,	1806m	51.6 (51.9)	4.6 (3.6)	
$[WRh(\mu\text{-}CMe)(CO)_2(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (VIIb)	Black	75	1984s,	1809m	48.8 (48.9)	3.7 (3.5)	
$[WRh(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)_2\{HB(pz)_3\}][PF_6]$ (VIIc)	Black	75	1971s,	1802m	48.8 (49.7)	4.0 (3.6)	5.9 (6.3)
$[WRh(\mu\text{-}CMe)(CO)_2(PPh_3)_2\{HB(pz)_3\}][PF_6]$ (VIId)	Dark green	80	1967s,	1804m	47.8 (47.0)	3.7 (3.5)	7.0 (6.7)
$[WRh(\mu\text{-}CMe)(CO)_2(cod)\{HB(pz)_3\}][BF_4]$ (VIII)	Black	70	1962s,	1795m	31.6 (32.4)	3.4 (3.1)	10.7 (10.8)
$[WRh\{\mu\text{-}\sigma:\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PPh_3)_2(\eta\text{-}C_5H_5)]$ (IX)	Brown	50	1971s,	1877m	59.5 (59.1)	4.4 (4.2)	
$[WRh(\mu\text{-}CC_6H_4Me\text{-}4)(H)_2(CO)_2(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (X)	Orange-yellow	90	1987s,	1803m	51.5 (51.8)	4.0 (3.7)	
$[WRh(\mu\text{-}CMe)(\mu\text{-}I)(\mu\text{-}CO)(CO)(PPh_3)_2\{HB(pz)_3\}]$ (XIa)	Brown	70	1932s,	1784m	47.3 (47.7)	4.0 (3.5)	7.2 (6.8)
$[WRh(\mu\text{-}CMe)(\mu\text{-}I)(\mu\text{-}CO)(CO)(cod)\{HB(pz)_3\}]$ (XIb)	Dark red	60	1922s,	1741m	30.9 (30.8)	3.2 (3.1)	10.9 (10.3)

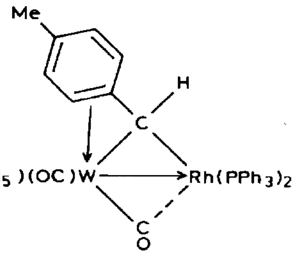
[a] Measured in CH_2Cl_2.

Table 2

NMR data [a]

Compound	$\delta(^{1}H)$ [b]	$\delta(^{13}C)$ [c]	$\delta(^{31}P)$ [d,e]
VIIa	2.44 (s, 3H, Me-4), 5.47 (s, 5H, C_5H_5), 7.12–7.35 (m, 34H, C_6H_4 and Ph)	356.8 (br, μ-C), 233.7 [d, CO, J(RhC) 13], 151.2–127.4 (C_6H_4 and Ph), 89.5 (C_5H_5), 21.9 (Me-4)	[f] 38.9 [d, J(RhP) 161]
VIIb	3.26 (s, 3H, Me), 5.56 (s, 5H, C_5H_5), 7.17–7.57 (m 30H, Ph)	362.0 (br, μ-C), 224.4 [d, CO, J(RhC) 12], 133.2–127.1 (Ph), 93.1 (C_5H_5), 40.8 (Me)	37.0 [d, J(RhP) 156]
VIIc	2.37 (s, 3H, Me-4), 6.30 (s, 3H, $C_3H_3N_2$), 7.50–7.92 (m, 40H, $C_3H_3N_2$, C_6H_4 and Ph)	237.1 [d, CO, J(RhC) 15], 146.5–126.9 ($C_3H_3N_2$, C_6H_4 and Ph), 22.1 (Me-4)	38.7 [d, J(RhP) 165]
VIId	[f] 2.40 (s, 3H, Me), 7.19–7.95 (m, 39H, $C_3H_3N_2$ and Ph)	346.1 [d, μ-C, J(RhC) 28], 233.2 [d, CO, J(RhC) 13], 144.3–106.6 ($C_3H_3N_2$ and Ph), 45.1 (Me)	44.8 [d, J(RhP) 161]
VIII	[f] 2.30 (m, 8H, CH_2), 3.01 (s, 3H, Me), 4.89–5.01 (m, 4H, CH), 6.21–7.98 (m, 9H, $C_3H_3N_2$)	338.2 [d, μ-C, J(RhC) 30], 232.1 [d, CO, J(RhC) 17], 144.5–94.0 ($C_3H_3N_2$ and cod), 40.5 (Me)	
IX	[f] 2.25 (s, 3H, Me-4), 5.10 (s, 5H, C_5H_5), 7.06–7.54 (m, 34H, C_6H_4 and Ph), 10.05 (m, 1H, μ-CH)	224.2 [CO, J(WC) 160], 194.1 [d, μ-C, J(RhC) 29, J(WC) 166], 151.1 [$C^4(C_6H_4)$], 132.7–121.2 (C_6H_4 and Ph), 114.4 [$C^1(C_6H_4)$], 94.0 [$C^2(C_6H_4)$], 89.5 (C_5H_5), 22.7 (Me-4)	[f] 29.0 [d, J(RhP) 127]
X	−10.50 [d of t, 2H, J(PH) 27, J(RhH) 16], 2.37 (s, 3H, Me-4), 4.99 (s, 5H, C_5H_5), 7.10–7.61 (m, 34H, C_6H_4 and Ph)	368.2 (m, μ-C), 240.8 [d, CO, J(RhC) 17], 151.5–129.0 (C_6H_4 and Ph), 89.6 (C_5H_5), 22.4 (Me-4)	[f] 27.3 [d, J(RhP) 146]
XIa	[f] 2.70 (s, 3H, Me), 6.31–7.98 (m, 39H, $C_3H_3N_2$ and Ph)	303.7 [d, μ-C, J(RhC) 30], 228.2 (br, CO), 222.4 [CO, J(WC) 167], 145.1–127.3 ($C_3N_3N_2$ and Ph), 105.4 ($C_3H_3N_2$), 40.5 (Me)	39.6 [d, J(RhP) 176]
XIb	[f] 2.21 (m, 8H, CH_2), 2.82 (s, 3H, Me), 4.81 (m, 4H, CH), 6.30–7.89 ($C_3H_3N_2$)	294.7 [d, μ-C, J(RhC) 27], 229.4 [d, CO, J(RhC) 12], 222.5 [CO, J(WC) 160], 144.6–106.3 ($C_3H_3N_2$), 104.1–97.4 (cod), 42.3 (Me)	

[a] Chemical shifts (δ) in ppm, coupling constants in Hz, spectra measured at room temperature. [b] Measured in CD_2Cl_2, unless otherwise stated. [c] Hydrogen-1 decoupled, measured in CD_2Cl_2/CH_2Cl_2. Chemical shifts are positive to high frequency of $SiMe_4$. [d] Hydrogen-1 decoupled, measured in CD_2Cl_2, unless otherwise stated. Chemical shifts are rel. to 85% H_3PO_4 (external). [e] In the PF_6^- salts there is a characteristic resonance for the anion at ca. δ −145, appearing as a heptet J(FP) ca. 700 Hz. [f] Measured in $CDCl_3$.



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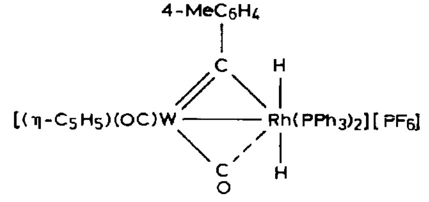

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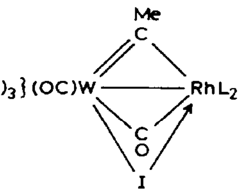
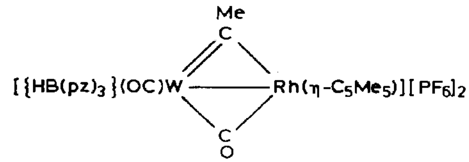
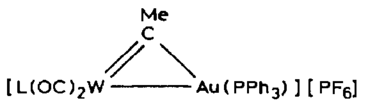


	L_2
XIa	2 × PPh_3
XIb	cod



(XII)



	L
XIIIa	$HB(pz)_3$
XIIIb	η-C_5H_5

dynamic behaviour in solution of the complex $[WRh(\mu\text{-}CR)(CO)_2(PPh_3)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ and related species [7*]. This takes the form of site-exchange of CO groups and rotation of the $Rh(PPh_3)_2$ fragment about an axis through the rhodium and the mid-point of the ligating C≡W group. It seems likely that similar behaviour occurs in solution with VII and VIII.

Treatment of a thf solution of VIIa with KH affords the neutral complex $[WRh\{\mu\text{-}\sigma:\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PPh_3)_2(\eta\text{-}C_5H_5)]$ (IX) (Table 1). Based on earlier work by ourselves [4b,10], and by others [11], including X-ray diffraction studies, it seems likely that in IX the μ-$CH(C_6H_4Me\text{-}4)$ group adopts a bonding mode in which three carbon atoms of the CC_6H_4 fragments ligate the tungsten atom so that it acquires an 18 electron configuration. In the ^1H NMR spectrum of IX the resonance at δ 10.05 is ascribed to that of the μ-CH group. It is somewhat more deshielded than the peaks for this moiety in the ^1H NMR spectra of the complexes $[WPt\{\mu\text{-}\sigma:\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PR_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (R = Me or Ph) which occur at ca. δ 6.7 [10]. The presence of the μ-$CH(C_6H_4Me\text{-}4)$ nucleus is clearly indicated in the ^{13}C $\{^1H\}$ NMR spectrum of IX by a peak at δ 194.1 ppm which appears as a doublet [J(RhC) 29 Hz], with ^{183}W satellites [J(WC) 166 Hz]. The observation of both ^{103}Rh– and ^{183}W–^{13}C coupling on this signal confirms the assignment.

We were unable to isolate products similar to IX by treating the species VIIb–VIId with KH or $NaBH_4$. Reactions were observed leading to decomposition, and there was some evidence of hydride attack at the $HB(pz)_3$ ligand of VIIc, rather than at the μ-CC_6H_4Me-4 group.

Compound VIIa reacts readily with molecular hydrogen to give the dihydrido complex $[WRh(\mu\text{-}CC_6H_4Me\text{-}4)(H)_2(CO)_2(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (X) but a similar reaction with VIIc seemed to result in loss of a PPh_3 group and the product could not be characterised. However, the ^{1}H NMR spectrum showed a high-field resonance at δ −12.8, appearing as a doublet of doublets due to coupling with a $RhPPh_3$ group [J(PH) 20, J(RhH) 12 Hz].

The spectroscopic data for X are in accord with the proposed structure. In the IR spectrum there are two CO stretching bands (Table 1), that at 1803 cm^{-1} suggesting one of the ligands is semi-bridging the W–Rh bond. In addition, an IR absorption at 2026 cm^{-1} is ascribed to a Rh–H stretch. In the ^{1}H NMR spectrum (Table 2) the high-field resonance at δ −10.50 appears as a doublet of triplets [J(PH) 27, J(RhH) 16 Hz], as expected for a *trans*-RhH_2 and *cis*-$Rh(PPh_3)_2$ arrangement. The ^{31}P {^{1}H} NMR spectrum shows a doublet signal [J(RhP) 146 Hz], the observation of one peak implying dynamic behaviour. The ^{13}C {^{1}H} NMR spectrum reveals a resonance for the μ-C nucleus at δ 368.2 ppm. Although the deshielding of this signal is comparable with those in the spectra of VII and VIII, different effects may be responsible, since complex X is a Rh^{III} compound. Only one CO peak is observed in the ^{13}C {^{1}H} NMR spectrum of X, and evidently again site-exchange of the two CO ligands must occur.

Treatment of VIIc and VIII with NaI affords, respectively, the iodo complexes $[WRh(\mu\text{-}CMe)(\mu\text{-}I)(\mu\text{-}CO)(CO)L_2\{HB(pz)_3\}]$ [$L_2 = 2 \times PPh_3$ (XIa) or cod (XIb)], data for which are given in Tables 1 and 2. Both products display the expected two bands in their IR spectra in the CO stretching region, but the absorptions at 1784 cm^{-1} (XIa) and 1741 cm^{-1} (XIb) strongly suggest that in each compound one carbonyl ligand bridges the W–Rh bond. This is supported by the observation of two CO resonances in the ^{13}C {^{1}H} NMR spectra; with, in the case of XIb, one resonance (δ 229.4) being a doublet [J(RhC) 12 Hz]. The resonances for the μ-C nuclei at δ 303.7 (XIa) and 294.7 ppm (XIb) are significantly less deshielded than those of the corresponding signals in the ^{13}C {^{1}H} NMR spectra of VII and VIII. This would be in accord with the species XI being electronically saturated [9] as formulated, with an iodo-bridge supporting the metal–metal bond and each metal having a closed 18 valence electron shell.

We have also studied the reaction between $[W(\equiv CMe)(CO)_2\{HB(pz)_3\}]$ and the salt $[Rh(NCMe)_3(\eta\text{-}C_5Me_5)][PF_6]_2$ in order to obtain a W–Rh di-cationic complex. The product $[WRh(\mu\text{-}CMe)(\mu\text{-}CO)(CO)(\eta\text{-}C_5Me_5)\{HB(pz)_3\}][PF_6]_2$ (XII) was unfortunately very insoluble in all organic solvents, and hence its ^{13}C {^{1}H} NMR spectrum could not be measured. Nevertheless, satisfactory analytical data were obtained (see Experimental section) and the ^{1}H NMR spectrum showed the expected peaks. The IR spectrum of XII showed two CO bands at 2016 and 1819 cm^{-1}, the latter indicating the presence of a bridging or semi-bridging carbonyl group.

The tungsten-gold compound $[WAu(\mu\text{-}CMe)(CO)_2(PPh_3)\{HB(pz)_3\}][PF_6]$ (XIIIa) was also prepared by treating $[W(\equiv CMe)(CO)_2\{HB(pz)_3\}]$ with $[AuCl(PPh_3)]$ in the presence of $TlPF_6$. Compound XIIIa was characterised by the data given in the Experimental section. In particular, the $^{13}C\ \{^1H\}$ NMR spectrum showed a resonance for the *C*Me nucleus at δ 280.8 ppm [d, *J*(PC) 47, *J*(WC) 140 Hz]. The observed chemical shift may indicate that the ethylidyne group semi-bridges the W–Au bond [7a]. Compound XIIIa is evidently more stable than the previously prepared complex $[WAu(\mu\text{-}CMe)(CO)_2(PPh_3)(\mu\text{-}C_5H_5)][PF_6]$ (XIIIb) which readily disproportionates in solution to give $[W_2Au(\mu\text{-}CMe)_2(CO)_4(\eta\text{-}C_5H_5)_2][PF_6]$ and $[Au(PPh_3)_2][PF_6]$ [8b]. The enhanced stability of XIIIa towards dissociation is probably due to the $HB(pz)_3$ ligand focusing electron density at the tungsten, the C_5H_5 group being a weaker σ donor.

Experimental

All experiments were carried out under oxygen-free nitrogen, using Schlenk tube techniques. Light petroleum refers to that fraction of b.p. 40–60 °C. The compounds $[W(\equiv CR)(CO)_2L]$ ($R = Me$ or $C_6H_4Me\text{-}4$, $L = \eta\text{-}C_5H_5$ [12]; $R = Me$ or $C_6H_4Me\text{-}4$, $L = HB(pz)_3$ [5]), $[Rh(PPh_3)_2(cod)][PF_6]$ [13], and $[Rh(NCMe)_3(\eta\text{-}C_5Me_5)][PF_6]_2$ [14] and $[AuCl(PPh_3)]$ [15], were prepared by methods described in the literature. Spectroscopic measurements were made with instrumentation listed previously [2]. Data for the new compounds VII–XI are given in Tables 1 and 2, that for XII and XIIIa are given below.

Synthesis of the complexes $[WRh(\mu\text{-}CR)(CO)_2(PPh_3)_2L][PF_6]$ *[*$R = C_6H_4Me\text{-}4$ *or Me,* $L = \eta\text{-}C_5H_5$ *or* $HB(pz)_3$*]*

(*i*) A CH_2Cl_2 (15 cm^3) solution of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.19 g, 0.46 mmol) was treated with solid $[Rh(PPh_3)_2(cod)][PF_6]$ (0.40 g, 0.46 mmol). After stirring the mixture for 1 h at room temperature, the volume of solvent was reduced in vacuo to ca. 2 cm^3, and Et_2O (20 cm^3) was added affording black microcrystals of $[WRh(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (VIIa) (0.49 g).

(*ii*) Similarly, $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ (0.08 g, 0.24 mmol) and $[Rh(PPh_3)_2(cod)][PF_6]$ (0.21 g, 0.24 mmol) in CH_2Cl_2 (10 cm^3) gave black microcrystals of $[WRh(\mu\text{-}CMe)(CO)_2(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (VIIb) (0.20 g). Crystals may be grown from CH_2Cl_2/Et_2O (1/5).

(*iii*) A toluene (5 cm^3) solution of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$ (0.07 g, 0.13 mmol) was treated with $[Rh(PPh_3)_2(cod)][PF_6]$ (0.11 g, 0.13 mmol), and the mixture was refluxed for 30 min. Solvent was removed in vacuo, and the black residue was crystallised from CH_2Cl_2/Et_2O (20 cm^3, 1/4) yielding black crystals of $[WRh(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)_2\{HB(pz)_3\}][PF_6]$ (VIIc).

(*iv*) Similarly, refluxing (30 min) a mixture of $[W(\equiv CMe)(CO)_2\{HB(pz)_3\}]$ (0.05 g, 0.10 mmol) and $[Rh(PPh_3)_2(cod)][PF_6]$ (0.09 g, 0.10 mmol) in toluene (6 cm^3) gave green microcrystals of $[WRh(\mu\text{-}CMe)(CO)_2(PPh_3)_2\{HB(pz)_3\}]$ (VIId) (0.10 g).

Synthesis of the complex $[WRh(\mu\text{-}CMe)(CO)_2(cod)\{HB(pz)_3\}][BF_4]$

A thf (5 cm^3) solution of $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ (0.08 g, 0.15 mmol) was treated with $AgBF_4$ (0.06 g, 0.30 mmol), to generate $[Rh(thf)_2(cod)][BF_4]$ in situ. After 5 min, solvent was removed in vacuo, and the yellow residue was extracted with CH_2Cl_2

(3×5 cm^3) and the extracts were filtered through a Celite column (2.5×10 cm). The resulting yellow solution was treated with [W(≡CMe)(CO)$_2${HB(pz)$_3$}] (0.14 g, 0.30 mmol) in CH_2Cl_2 (5 cm^3). The colour changed immediately from yellow to dark red. After stirring for 15 min, solvent was reduced in vacuo to a volume of ca. 2 cm^3, and Et_2O (15 cm^3) was added slowly to give black microcrystals of [WRh(μ-CMe)(CO)$_2$(cod){HB-(pz)$_3$}][BF$_4$] (VIII) (0.08 g).

Reactions of the complexes [WRh(μ-CR)(CO)$_2$(PPh$_3$)$_2$L][PF$_6$]

(*i*) A thf (8 cm^3) solution of VIIa (0.06 g, 0.05 mmol) was treated with KH (0.01 g, 0.24 mmol) suspended in thf (5 cm^3). There was an immediate colour change from dark green to red brown. After stirring at room temperature for 15 min, solvent was removed in vacuo, and the residue was extracted with CH_2Cl_2 (3×5 cm^3). The extracts were filtered through a Celite column (2.5×5 cm). Reduction in volume of solvent in vacuo to ca. 5 cm^3, followed by addition of light petroleum (15 cm^3) gave a brown precipitate. Solvent was removed in vacuo, and the precipitate was washed with light petroleum (3×5 cm^3) and dried in vacuo to give brown microcrystals of [WRh{μ-CH(C$_6$H$_4$Me-4)}(CO)$_2$(PPh$_3$)$_2$(η-C$_5$H$_5$)] (IX) (0.03 g).

(*ii*) A thf (15 cm^3) solution of (VIIa) (0.10 g, 0.08 mmol) was treated with a stream of hydrogen at room temperature and 1 atm. After 30 min the volume of solvent was reduced in vacuo to ca. 2 cm^3, and Et_2O (10 cm^3) was slowly added to afford a yellow orange product. Removal of the solvent in vacuo gave orange microcrystals of [WRh(μ-CC$_6$H$_4$Me-4)(H)$_2$(CO)$_2$(PPh$_3$)$_2$(η-C$_5$H$_5$)][PF$_6$] (X) (0.09 g).

(*iii*) Compound (VIId) (0.12 g, 0.10 mmol) in thf (10 cm^3) was treated with NaI (0.02 g, 0.13 mmol). After stirring the mixture for 15 min, solvent was removed in vacuo, and the residue was extracted with CH_2Cl_2 (3×5 cm^3). The extracts were filtered through Celite (2.5×10 cm). Solvent was removed in vacuo, and the residue crystallised from Et_2O/light petroleum (30 cm^3, 1/5) to afford a brown product which was washed with light petroleum (3×2 cm^3) to give after drying under vacuum, microcrystals of [WRh(μ-CMe)(μ-I)(μ-CO)(CO)(PPh$_3$)$_2${HB(pz)$_3$}] (XIa) (0.09 g).

In a similar reaction, compound VIII (0.05 g, 0.06 mmol) and NaI (0.02 g, 0.10 mmol) afforded the dark red product [WRh(μ-CMe)(μ-I)(μ-CO)(CO)(cod){HB-(pz)$_3$}] (XIb) (0.03 g).

Reaction between [Rh(NCMe)$_3$(η-C$_5$Me$_5$)][PF$_6$]$_2$ and [W(≡CMe)(CO)$_2${HB(pz)$_3$}]

Solid [Rh(NCMe)$_3$(η-C$_5$Me$_5$)][PF$_6$]$_2$ (0.04 g, 0.08 mmol) was added to a CH_2Cl_2 (10 cm^3) solution of [W(≡CMe)(CO)$_2${HB(pz)$_3$}] (0.04 g, 0.08 mmol). The dark red solution obtained was stirred for 90 min at room temperature. Solvent was removed in vacuo and the black residue was crystallised from CH_2Cl_2/Et_2O (12 cm^3, 1/5). The product was washed with Et_2O (3×5 cm^3) and dried under vacuum to give black microcrystals of [WRh(μ-CMe)(μ-CO)(CO)(η-C$_5$Me$_5$){HB(pz)$_3$}][PF$_6$]$_2$ (XII) (0.06 g, 77%) (Found: C, 27.4; H, 3.3; N, 8.8. $C_{23}H_{28}BF_{12}N_6O_2P_2RhW$ calc: C, 27.4; H, 2.8; N, 8.3%); ν_{max}(CO) at 2016s, and 1819 cm^{-1} (in CH_2Cl_2). NMR: ^1H (CD_2Cl_2), δ 2.17 (s, 15 H, C_5Me_5), 2.98 (s, 3 H, Me), and 6.45–7.99 (m, 9 H, $C_3H_3N_2$).

Synthesis of the salt [WAu(μ-CMe)(CO)$_2$(PPh$_3$){HB(pz)$_3$}][PF$_6$]

A thf (10 cm^3) solution of [W(≡CMe)(CO)$_2${HB(pz)$_3$}] (0.05 g, 0.10 mmol) was treated with solid [AuCl(PPh$_3$)] (0.05 g, 0.10 mmol) and TlPF$_6$ (0.04 g, 0.10 mmol). The mixture was stirred for 30 min at room temperature giving an orange solution and a white precipitate assumed to be TlCl. Solvent was removed in vacuo and the yellow residue was extracted with CH_2Cl_2 (3 × 5 cm^3), and the extracts were filtered through Celite (2.5 × 5 cm^3). Removal of solvent in vacuo, and crystallisation from Et_2O (20 cm^3) yielded yellow crystals of [WAu(μ-CMe)(CO)$_2$(PPh$_3$){HB-(pz)$_3$}][PF$_6$] (XIIIa) (0.08 g, 75%) (Found: C, 34.7; H, 2.7; N, 7.7. $C_{31}H_{28}AuBF_6N_6O_2P_2W$ calc: C, 34.3; H, 2.6; N, 7.7%); ν_{max}(CO) at 2025vs and 1946vs cm^{-1} (in CH_2Cl_2). NMR: ^1H ($CDCl_3$), δ 2.40 (s, 3H, Me), 6.31 (m, 3H, $C_3H_3N_2$), 7.26 (m, 19H, $C_3H_3N_2$ and Ph), and 7.84 (m, 2H, $C_3H_3N_2$); ^{13}C {^1H} (CD_2Cl_2/CH_2Cl_2), δ 280.8 [d, μ-C, *J*(PC) 47, *J*(WC) 140], 213.6 [CO, *J*(WC) 163 Hz], 146.3–129.9 ($C_3H_3N_2$ and Ph), and 40.9 ppm (Me); ^{31}P {^1H} ($CDCl_3$), δ 47.8 ppm.

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References

1 F.G.A. Stone, Pure and Appl. Chem., 58 (1986) 529; "Inorganic Chemistry: Toward the 21st Century", M.H. Chisholm (Ed.), ACS Symp. Ser., 211 (1983) 383.

2 For recent work in this area see G.P. Elliott, J.A.K. Howard, T. Mise, C.M. Nunn, and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1987) 2189; S.J. Davies, G.P. Elliott, J.A.K. Howard, C.M. Nunn, and F.G.A. Stone, ibid., (1987) 2177.

3 M.J. Chetcuti, P.A.M. Chetcuti, J.C. Jeffery, R.M. Mills, P. Mitrprachachon, S.J. Pickering, F.G.A. Stone, and P. Woodward, J. Chem. Soc., Dalton Trans., (1982) 699.

4 (a) J.A. Abad, L.W. Bateman, J.C. Jeffery, K.A. Mead, H. Razay, F.G.A. Stone, and P. Woodward, J. Chem. Soc., Dalton Trans., (1983) 2075; (b) J.C. Jeffery, C. Sambale, M.F. Schmidt, and F.G.A. Stone, Organometallics, 1 (1982) 1597; (c) M. Green, J.C. Jeffery, S.J. Porter, H. Razay, and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1982) 2475; (d) J.C. Jeffery, C. Marsden, and F.G.A. Stone, ibid., (1985) 1315.

5 M. Green, J.A.K. Howard, A.P. James, C.M. Nunn, and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1986) 187.

6 M.D. Bermudez, E. Delgado, G.P. Elliott, N.H. Tran-Huy, F. Mayor-Real, F.G.A. Stone, and M.J. Winter, J. Chem. Soc., Dalton Trans., (1987) 1235.

7 (a) For the synthesis of complexes with W–Rh bonds obtained from the salts [N(PPh$_3$)$_2$][W(≡CC$_6$H$_4$Me-4)(CO)$_2$(η^5-$C_2B_9H_9R_2$)] (R = H or Me), see M. Green, J.A.K. Howard, A.P. James, C.M. Nunn, and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1987) 61. (b) Other species with W–Rh bonds have been prepared by treating the complex [ReW(≡CC$_6$H$_4$Me-4)(CO)$_9$] with [Rh(CO)$_2$(η^5-C_9H_7)], see J.A. Abad, E. Delgado, M.E. Garcia, M.J. Grosse-Ophoff, I.J. Hart, J.C. Jeffery, M.S. Simmons, and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1987) 41.

8 (a) M. Müller-Gliemann, S.V. Hoskins, A.G. Orpen, A.L. Ratermann, and F.G.A. Stone, Polyhedron, 5 (1986) 791; (b) G.A. Carriedo, J.A.K. Howard, F.G.A. Stone, and M.J. Went, J. Chem. Soc., Dalton Trans., (1984) 2545; (c) G.A. Carriedo, J.A.K. Howard, K. Marsden, F.G.A. Stone, and P. Woodward, ibid., (1984) 1589.

9 M. Green, J.A.K. Howard, A.P. James, A.N. de M. Jelfs, C.M. Nunn, and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1986) 1697; S.J. Dossett, A.F. Hill, J.C. Jeffery, F. Marken, P. Sherwood, and F.G.A. Stone, ibid., in press.

10 J.C. Jeffery, J.C.V. Laurie, I. Moore, H. Razay, and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1984) 1563.

11 L. Messerle and M.D. Curtis, J. Am. Chem. Soc., 102 (1980) 7789; M.D. Curtis, L. Messerle, J.J. D'Errico, H.E. Solis, J.D. Barcelo, and W.M. Butler, ibid., 109 (1987) 3603.

12 E.O. Fischer, T.L. Lindner, G. Huttner, P. Friedrich, F.R. Kreissl, and J.O. Besenhard, Chem. Ber., 110 (1977) 3397; W. Uedelhoven, K. Eberl, and F.R. Kreissl, ibid., 112 (1979) 3376.

13 R.R. Schrock and J.A. Osborn, J. Am. Chem. Soc., 93 (1971) 2397.

14 C. White, S.J. Thompson, and P.M. Maitlis, J. Chem. Soc., Dalton Trans., (1977) 1654.

15 F.G. Mann, A.F. Wells, and D. Purdie, J. Chem. Soc., (1971) 93.