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Reactions of the hetero-metallic complexes $[WReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{15}]$ and $[ReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{10}]$ with secondary and tertiary phosphines

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Abstract

Reaction of the complex $[WReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{15}]$ with PMe_2Ph gives a mixture of the mono- and bis-phosphine complexes $[WReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{15-x}(PMe_2Ph)_x]$ ($x = 1$ or 2), whilst that with the bidentate phosphine $Ph_2PCH_2PPh_2$ (dppm) affords $[WReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{13}(Ph_2PCH_2PPh_2)]$. In contrast, reaction with two equivalents of the secondary phosphine PPh_2H gives the phosphido-bridged derivative $[WCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}PPh_2)(CO)_8(PPh_2H)]$. Formation of the latter WCo_2 complex involves formal loss of $[ReH(CO)_5]$ and a mechanism for this process is discussed. Treatment of the related $ReCo_2$ compound $[ReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{10}]$ with dppm affords the mono- and bis-dppm derivatives $[ReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(Ph_2PCH_2PPh_2)]$ and $[ReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_x(Ph_2PCH_2PPh_2)_2]$ ($x = 6$ or 7) respectively. As previously reported, treatment of $[ReCr(\equiv CC_6H_4Me\text{-}4)(CO)_9]$ with $[Co_2(CO)_8]$ gives $[CrReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{15}]$, which thermally rearranges to $[ReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{10}]$. The new complexes $[Re_2Co_2\{\mu\text{-}(RCCR)\}(CO)_{12}]$ and $[CrReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{13}]$ have been identified as by-products in the latter reactions. Spectroscopic data for the new compounds are reported and discussed in the context of the structures proposed.

Introduction

We have previously shown that treatment of the terminal alkylidyne compounds $[ReM(\equiv CC_6H_4Me\text{-}4)(CO)_9]$ (M = W, Mo or Cr) with $[Co_2(CO)_8]$ affords the tetranuclear metal complexes $[MReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{15}]$ (Ia–Ic), which on thermolysis in toluene (111° C) are converted to the rheniumdicobalt complex $[ReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{10}]$ (II) [1]. It has also been shown that treatment of the terminal alkylidyne complex $[CoW(\equiv CC_6H_4Me\text{-}4)(CO)_8]$ with $[Fe_2(CO)_9]$ af-

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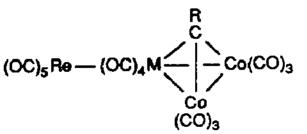
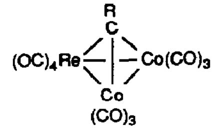
fords $[Fe_2Co(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_9]$, and some reactions of this complex with PPh_3 and $Ph_2PCH_2PPh_2$ (dppm) have been investigated [2]. Related reactions



(Ia) M = W
(Ib) M = Mo
(Ic) M = Cr



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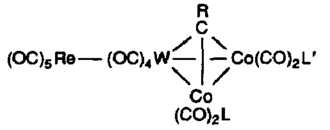
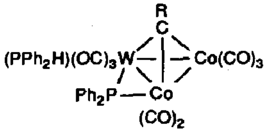
of the clusters $[WCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$ [3] and $[MFe_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ (M = W or Mo) [4,5] with monodentate and bidentate tertiary phosphine ligands have also been studied, and it has been shown that with secondary phosphine ligands phosphido-bridged derivatives may be obtained [6–8]. We report here the reactions of complexes Ia and II with PMe_2Ph, $Ph_2PCH_2PPh_2$ and PPh_2H. The results obtained reveal some interesting contrasts with the behaviour of related μ_3-alkylidyne complexes.

Results and discussion

Treatment of $[WReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{15}]$ (Ia), with one equivalent of PMe_2Ph in dilute diethyl ether solution gave poor yields (~ 10%) of the mono-substituted PMe_2Ph derivative III, a moderate yield (~ 30%) of the bis-PMe_2Ph complex IV, and appreciable amounts of unchanged Ia. Evidently III reacts readily with a second molecule of PMe_2Ph to give IV, and the latter complex was obtained in good yield when Ia was treated with two equivalents of PMe_2Ph. The related reaction of Ia with one equivalent of the bidentate phosphine dppm gave V.



(III) L = CO, L' = PMe_2Ph
(IV) L = L' = PMe_2Ph
(V) LL' = $Ph_2PCH_2PPh_2$



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Compounds III, IV and V were characterised by microanalysis and by their ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR data (Tables 1 and 2). Their ^1H NMR spectra show the expected resonances for the PMe_2Ph or dppm ligands and for the $\mu_3\text{-}CC_6H_4Me\text{-}4$ groups. In the $^{31}P\{^1H\}$ NMR spectra the broad resonances observed are consistent with phosphorus ligands attached to cobalt, and the observation of a single $^{31}P\{^1H\}$ resonance for complexes IV and V confirms the symmetric structures shown, which have phosphorus ligands at both cobalt centres. The $^{13}C\{^1H\}$ NMR spectra of IV and V closely resemble that of the parent complex Ia [1]. They show characteristic μ_3-CR resonances at δ 257.9 (IV) and 259.5 (V) ppm, singlet resonances for the four equivalent equatorial carbonyl ligands on tungsten, and two singlets in 1/4 ratio for the axial and equatorial carbonyl ligands of the $Re(CO)_5$ groups. The observation of single resonances for the equatorial $W(CO)_4$ and $Re(CO)_4$ carbonyl ligands con-

Table 1

Analytical and physical data for the complexes

Compound [a]	Colour	Yield (%)	ν_{max}(CO) (cm^{-1})	Analysis (Found (calc)(%))	
				C	H
[WReCo$_2$(μ_3-CR)(CO)$_{14}$(PMe$_2$Ph)] [b] (III)	Green	10	[c] 2110m, 2062m, 2056m, 2021s, 2010m, 1981m, 1937w, 1927w	–	–
[WReCo$_2$(μ_3-CR)(CO)$_{13}$(PMe$_2$Ph)$_2$] (IV)	Green	70	[c] 2104m, 2051w, 2030w, 2011s, 1998m, 1977m, 1946w, 1893w br	36.0 (36.1)	2.4 (2.4)
[WReCo$_2$(μ_3-CR)(CO)$_{13}$(Ph$_2$PCH$_2$PPh$_2$)] (V)	Green	80	[c] 2106m, 2035w, 2013s, 1993w, 1979m, 1972m, 1970w, 1955w br	39.5 (41.3)	2.2 (2.2)
[WCo$_2$(μ_3-CR)(μ-PPh$_2$)(CO)$_8$(PPh$_2$H)] [d] (VI)	Green	60	[c] 2050m, 2006s, 1981m, 1932w br, 1897w br	46.9 (46.6)	2.8 (2.8)
[ReCo$_2$(μ_3-CR)(CO)$_8$(Ph$_2$PCH$_2$PPh$_2$)] (VII)	Black	63	[e] 2068s, 2056w, 2007s, 1996s, 1985m, 1976m, 1959w, 1939w	48.4 (48.5)	3.1 (2.9)
[ReCo$_2$(μ_3-CR)(CO)$_7$(Ph$_2$PCH$_2$PPh$_2$)$_2$] [f] (VIII)	Green	65	[e] 2034m, 1998s, 1975vs, 1958m sh, 1933m, 1916m, 1901w, 1891w sh	54.4 (54.8)	3.8 (3.6)
[ReCo$_2$(μ_3-CR)(CO)$_6$(Ph$_2$PCH$_2$PPh$_2$)$_2$] [f] (IX)	Orange	60	[g] 2065w, 2012m, 1985vs, 1947s br, 1906m, 1893 m sh, 1850w br, 1764w br, 1744w br	54.8 (54.6)	4.0 (3.7)
[Re$_2$Co$_2${μ-(RCCR)}(CO)$_{12}$] (X)	Brown	38	[e] 2089, 2071w, 2054vs, 2028s, 2024s, 2015m, 1977w	32.1 (32.6)	1.2 (1.4)
[CrReCo$_2$(μ_3-CR)(CO)$_{13}$] (XI)	Purple	9	[g] 2104w, 2061vs, 2049s, 2039m, 2010w, 2000w, 1990w, 1966s, 1902w br	30.5 (30.6)	1.2 (0.9)

[a] R = C_6H_4Me-4. [b] Compound failed to crystallise, see text. [c] In methylcyclohexane. [d] Crystallises with 0.5 CH_2Cl_2. [e] In n-hexane. [f] Crystallises with one molecule of CH_2Cl_2. [g] In CH_2Cl_2.

firms that, as in Ia, these groups are rotating rapidly about the Re–W axis on the NMR time scale [1].

We have previously reported related phosphine derivatives of the complexes [MFe$_2$(μ_3-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_8$(η-C$_5$H$_5$)] (M = W or Mo) [4,5] and

Table 2. ^{1}H, ^{13}C and ^{31}P NMR data [a] for the complexes

Compound	^{1}H (δ) [b,c]	^{13}C {^{1}H} (δ) [c,d]	^{31}P {^{1}H} (δ) [d,e]
III	1.57 [d, 3H, MeP, *J*(PH) 10], 1.67 [d, 3H, MeP, *J*(PH) 9], 2.38 (s, 3H, Me-4), 7.08, 7.25 [$(AB)_2$, 4H, C_6H_4, *J*(AB) 8], 7.4 (m, 5H, Ph)		4.1 (PMe_2Ph)
IV	1.50 [t, 6H, MeP, *J*(PH) 5], 1.54 [t, 6H, MeP, *J*(PH) 5], 2.34 (s, 3H, Me-4), 6.98, 7.49 [$(AB)_2$, 4H, C_6H_4, *J*(AB) 8], 7.4 (m, 10H, Ph)	257.9 (μ_3-C), 219.0 (br, WCO), 206.0 (br, CoCO), 193.8 (4 ReCO), 183.0 (ReCO), 160.1, 135.4 (C(1) and C(4) of C_6H_4 Me-4), 138.4–131.8 (C_6H_4 and Ph), 21.2 (Me-4), 18.2 [t, MeP, *J*(PC) 12], 16.4 [t, MeP, *J*(PC) 11]	3.6 (PMe_2Ph)
V	2.40 (s, 3H, Me-4), 3.29 [d of t, 1H, PCH_2P, *J*(HH) 12, *J*(PH) 12], 3.79 [d of t, 1H, PCH_2P, *J*(HH) 12, *J*(PH) 12], 6.61, 6.78 [$(AB)_2$, 4H, C_6H_4, *J*(AB) 8], 7.2 (m, 20H, Ph)	259.5 (μ_3-C), 215.1 [WCO, *J*(WC) 119], 210.8, 202.2 (CoCO), 193.1 (4 ReCO), 182.5 (ReCO) 161.0 (C(1) of C_6H_4 Me-4), 136.4–128.5 (C_6H_4 and Ph), 29.5 [t, PCH_2P, *J*(PC) 24], 21.3 (Me-4)	25.1 ($Ph_2PCH_2PPh_2$)
VI	2.12 (s, 3H, Me-4), 6.54, 6.77 [$(AB)_2$, 4H, C_6H_4, *J*(AB) 8], 7.17 [d of d, 1 H, PPh_2H, *J*(PH) 4, 367], 7.5 (m, 20H, Ph)	251.8 [d, μ_3-C, *J*(PC) 15], 205.2 (2 CoCO), 204.1 (3 CoCO), 205.6 [d, WCO, *J*(PC) 8, *J*(WC) 118], 155.0 [C(1) of C_6H_4], 143.7–124.5 (C_6H_4 and Ph), 19.9 (Me-4)	−9.2 [d, $WPPh_2H$, *J*(PP) 14, *J*(WP) 193], 226 (br, μ-PPh_2)
VII	2.30 (s, 3H, Me-4), 3.17 (m, 2H, PCH_2P), 6.65–7.40 (m, 20H, C_6H_4 and Ph)	298.4 (μ_3-C), 209.1, 204.8 (CoCO), 195.5 (br, ReCO), 157.7 (C(1) of C_6H_4), 137.4 (s, C(4) of C_6H_4), 136.2–127.2 (C_6H_4 and Ph), 25.2 [t, PCH_2P, *J*(PC) 27], 21.2 (Me-4)	33.7 ($Ph_2PCH_2PPh_2$)
VIII	2.23 (s, 3H, Me-4), 3.3 (m, 4H, PCH_2P), 6.5–7.6 (m, 44H, C_6H_4 and Ph)	286.2 [d, μ_3-C, *J*(PC) 10], 214.7–196.7 (v br, CoCO and ReCO), 160.7 (C(1) of C_6H_4), 138.9–127.6 (C_6H_4 and Ph), 32.7 [d of d, $RePCH_2P$, *J*(PC) 29, 35], 25.3 [t, $CoPCH_2PCo$, *J*(PC) 25], 21.1 (Me-4)	−25.9 [d, $\mathrm{RePCH_2}P$, *J*(PP) 59], 5.42 [d, $\mathrm{Re}P\mathrm{CH_2P}$, *J*(PP) 59], 32.5 (br, $\mathrm{Co}P\mathrm{CH_2}P\mathrm{Co}$)
IXa	2.19 (s, 3H, Me-4), 3.32–4.87 (m, 4H, PCH_2P), 6.31–7.34 (m, 44H, C_6H_4 and Ph)	[f] 160.2 (C(1) of C_6H_4), 136.7, 126.9 (C_6H_4 and Ph), 43.3 [t, PCH_2P, *J*(PC) 27], 37.0 [t, PCH_2P, *J*(PC) 18], 21.1 (Me-4)	−50.6 (s, $RePCH_2PRe$), −27.1 (s, $RePCH_2PRe$), 36.1 (br, $CoPCH_2PCo$)
X	2.32 (s, 6H, Me-4), 7.36 (m, 8H, C_6H_4)	198.9 (s, br, CO), 194.2–197.4 (m, CO), 192.8 (s, CO), 137.8 (C(1) of C_6H_4), 134.8 (C(4) of C_6H_4), 128.8 (m, C(2), C(3), C(5), C(6) of C_6H_4), 92.2 ($\mathit{C}C_6H_4$Me-4), 21.1 (Me-4)	

Table 2 (continued)

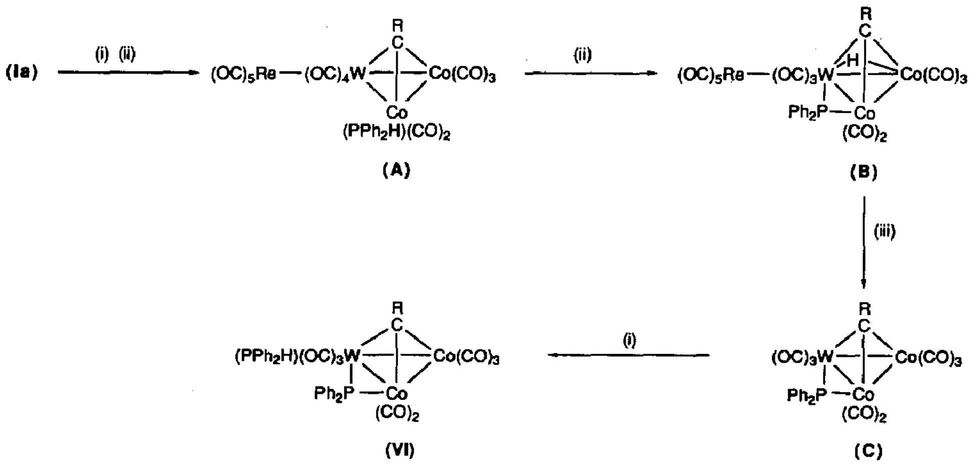
Compound	^1H (δ) [b,c]	^{13}C {^1H} (δ) [c,d]	^{31}P {^1H} (δ) [d,e]
XI	2.31 (s, 3H, Me-4), 5.56 (m, 4H, C_6H_4)	297.7 (μ_3-C), 230.9 [$Cr(CO)_3$], 194.8 [s, br, $Co(CO)_3$, $Re(CO)_4$], 125.7 (C(1) of C_6H_4), 112.9 (C(4) of C_6H_4), 88.4, 99.6 (2×s, C(2), C(3), C(5), C(6) of C_6H_4), 20.8 (Me-4)	

[a] Chemical shifts (δ) in ppm, coupling constants in Hz, measurements at ambient temperature. [b] Measured in CD_2Cl_2. [c] Positive chemical shifts to high frequency of $SiMe_4$. [d] Measured in CD_2Cl_2/CH_2Cl_2, ^1H decoupled. [e] Positive chemical shifts to high frequency of H_3PO_4 (external), [f] Peaks due to μ_3-CR and CO ligands not observed due to poor signal-noise ratio.

[$WCo_2(\mu_3$-CC_6H_4Me-4)$(CO)_7(\eta$-$C_5H_5)$] [3], and as for III, IV and V, addition of phosphorus ligands is found to occur exclusively at the first row (Fe or Co) transition metal centre. Treatment of the related cluster [$Co_3(\mu_3$-CMe)$(CO)_9$] with dppm gives [$Co_3(\mu_3$-CMe)(μ-dppm)$(CO)_7$], which exists as two isomers, with the dppm ligand adopting an axial [^{31}P {^1H} ca. δ 88 ppm] or an equatorial [^{31}P {^1H} ca. δ 35 ppm] orientation with respect to the plane of the three cobalt atoms [9,10]. The ^{31}P {^1H} NMR spectrum of V showed a resonance at 25.1 ppm, which is similar to that found for the equatorial isomer of [$Co_3(\mu_3$-CMe)(μ-dppm)$(CO)_7$].

We have previously noted that thermolysis of I (toluene, 111° C) leads to loss of a $M(CO)_x$ (M = W, Mo or Cr) fragment with formation of the heterotrimetallic $ReCo_2$ complex II [1]. In marked contrast we now find that treatment of Ia with two equivalents of PPh_2H under mild conditions (20° C) results in a formal loss of [$ReH(CO)_5$], and by chromatography the WCo_2 complex VI may be obtained in good yield. Complex VI was readily identified by its analytical and spectroscopic data (Tables 1 and 2). The ^{31}P {^1H} NMR spectrum was particularly informative. A sharp doublet at δ −9.2 ppm [J(PP) 14, J(WP) 193 Hz] may be assigned to a terminal PPh_2H ligand on tungsten which is coupled to a μ-PPh_2 group bridging a tungsten–cobalt bond (δ μ-P 226 ppm). The ^{13}C {^1H} NMR spectrum of VI showed a doublet at δ 251.8 ppm [J(PC) 15 Hz] for the μ_3-CR ligand and the ^1H NMR spectrum showed a doublet of doublets at 7.17 ppm [J(PH) 4, 367 Hz] which may be assigned to the $PPh_2\mathit{H}$ hydrogen atom.

Formation of VI was unexpected and involves formal loss of [$ReH(CO)_5$]. A possible mechanism for its formation is shown in Scheme 1. Initial attack of PPh_2H on Ia should give a terminal PPh_2H derivative **A**, analogous to the PMe_2Ph complex III. We have previously shown that the related terminal PPh_2H complexes [$WCo_2(\mu_3$-CR)$(CO)_7(PPh_2H)(\eta$-$C_5H_5)$] (R = Me or C_6H_4Me-4) and [$WFe_2(\mu_3$-CC_6H_4Me-4)(μ-CO)$(CO)_7(PPh_2H)(\eta$-$C_5H_5)$] rapidly rearrange under ambient conditions to the phosphido-bridged derivatives [$WCo_2(\mu$-H)(μ_3-CR)(μ-PPh_2)$(CO)_6(\eta$-$C_5H_5)$] and [$WFe_2(\mu$-H)(μ_3-CC_6H_4Me-4)(μ-PPh_2)$(CO)_7(\eta$-$C_5H_5)$] respectively [6–8]. It was therefore expected that **A** would rearrange to give a stable phosphido-bridged complex **B**. However attempts to isolate mono-phosphine substituted complexes via reaction of Ia with a single equivalent of PPh_2H gave only VI and unchanged Ia. Evidently **B**, if formed, readily undergoes reductive elimination of



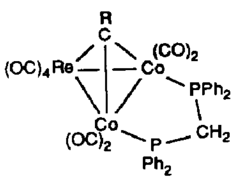
Scheme 1. R = C_6H_4Me-4; (i) PPh_2H, (ii) −CO, (iii) −[$ReH(CO)_5$].

[$ReH(CO)_5$] to give a coordinatively unsaturated intermediate C, which reacts with a further equivalent of PPh_2H to give VI.

The reaction of the $ReCo_2$ complex II with dppm was also examined in order to allow comparison with the related reactions of Ia. Under mild conditions II reacts rapidly with one equivalent of dppm to give the black derivatives VII. The ^{31}P {^1H} NMR spectrum shows a broad singlet at δ 33.7 ppm, which is consistent with the dppm ligand bridging the cobalt–cobalt bond. Moreover in the ^{13}C {^1H} NMR spectrum the μ_3-CR resonance occurs at δ 298.4 ppm, a shift very similar to that for the precursor II (δ μ-CR 297.9 ppm).

Compound VII slowly reacts with a further equivalent of dppm (24 h, Et_2O, 20 °C) to give a green crystalline precipitate of the bis-dppm complex VIII. The ^{31}P {^1H} NMR spectrum of VIII was especially informative, and showed a broad resonance at δ 32.50 ppm for the dppm ligand bridging the cobalt–cobalt bond and a pair of sharp doublets at δ −25.9 and 5.42 ppm [J(PP) 59 Hz] that may be assigned to a monodentate dppm ligand attached to the rhenium atom. Compound VIII is therefore closely related to the homonuclear cluster [$Co_3(\mu_3$-CMe)(μ-dppm)$(CO)_5$(dppm)], which also has both a bridging and a monodentate dppm ligand [10]. The latter Co_3 species thermally rearranges to give the bis-(μ-dppm) complex [$Co_3(\mu_3$-CMe)$(\mu$-dppm$)_2(CO)_5$] [9,10], and it was therefore of interest to see if the uncoordinated end of the mondentate dppm ligand in VIII could similarly be induced to coordinate to cobalt.

Refluxing a solution of VIII in THF for 2 h gave as the major product as comparatively insoluble orange complex IX. Interestingly, VIII readily rearranged to IX when its solutions were passed down an alumina chromatography column, whereas attempts to induce a similar rearrangement on a Florisil column led to complete decomposition. In the solid state IX appears to exist as a single orange isomer IXa, but in solution thin layer chromatography suggests that an equilibrium exists between a major orange IXa and a minor green IXb isomer. Consistently, the solution IR spectrum of IX showed nine bands, which is more than expected for a single isomer. Although the NMR spectra of IX also afforded some evidence for the presence of isomers, the poor signal to noise ratio prevented unambiguous assign-



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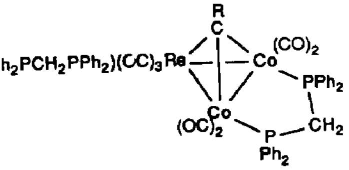

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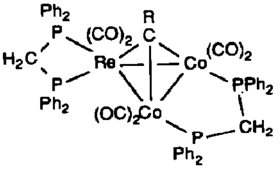

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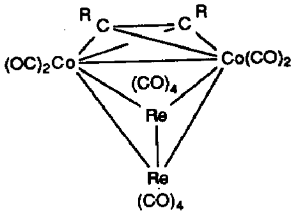

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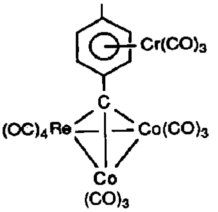
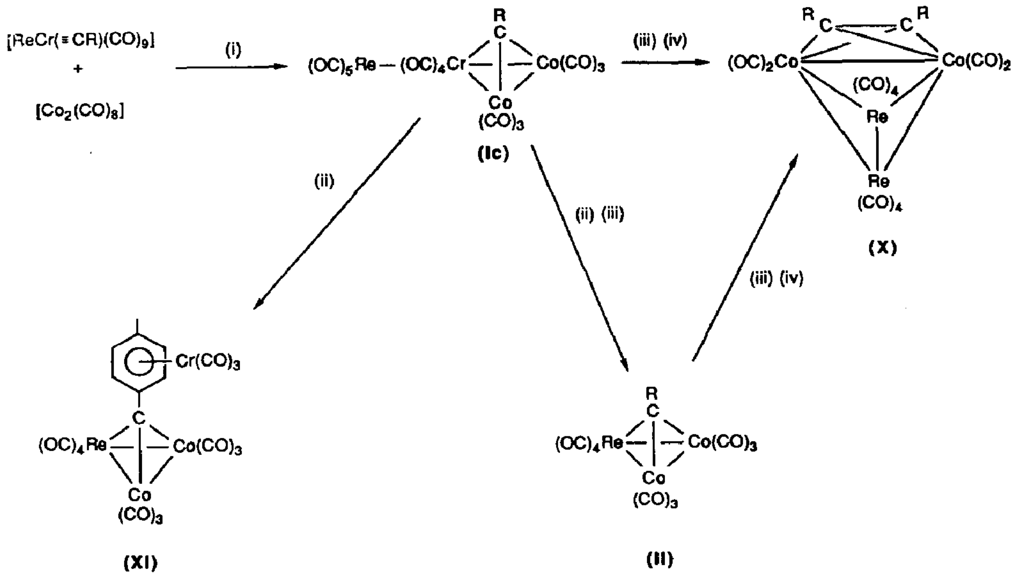


(XI)

ment of peaks associated with the minor green isomer. Only the NMR data for the predominant orange species IXa are therefore reported in Table 2. The ^1H NMR spectrum of IXa is very similar to that of VIII, and its ^{31}P $\{^1H\}$ NMR spectrum shows a broad resonance at δ 36.1 ppm, which suggests that the μ-dppm ligand present in the precursor VIII is retained in IX. The remaining dppm ligand shows relatively sharp and shielded resonances at δ -27.1 and -50.6 ppm. The absence of quadrupolar broadening by cobalt and the shielded chemical shifts observed lead us to assign these resonances tentatively to a chelating bidentate dppm ligand on rhenium.

The $ReCo_2$ complex II required for work described in this paper was prepared by thermolysis of the chromium complex Ic. The chromium complex was chosen because it had previously been observed that thermal elimination of a $Cr(CO)_x$ fragment for this complex occurred more rapidly than loss of $M(CO)_x$ ($M = W$ or Mo) from the analogous complexes Ia,Ib [1]. Whilst carrying out comparatively large scale preparations of Ic and subsequently converting it to II, we isolated two hitherto unidentified by-products (Scheme 2). Thus as previously reported, reaction of $[ReCr(\equiv CR)(CO)_9]$ with $[Co_2(CO)_8]$ gave the expected product Ic in ca. 60% yield, but a new Re_2Co_2 complex X was also isolated in moderate yield (ca. 38%). Compound X is extremely soluble even in non-polar solvents, and crystals suitable



Scheme 2. R = C_6H_4Me-4; (i) −2CO, (ii) Δ, (iii) $-Cr(CO)_x$, (iv) [ReCr(≡CR)$(CO)_9$].

for a single crystal X-ray diffraction study could not be obtained. However, a tentative structure may be assigned on the basis of its analytical and spectroscopic data. The ^{13}C $\{^1H\}$ NMR spectrum of X showed no peak for a μ_3-CR ligand. However a resonance at δ 92.2 ppm may be tentatively assigned to the ligated carbon atoms of a transversely bridging alkyne R*C*≡*C*R (R = C_6H_4Me-4), which is presumably formed via coupling of two CR ligands. The latter chemical shift is similar to that found for the transversely bridged alkynes in the complexes [Co_2(μ-Ph*C*≡*C*Ph)$(CO)_6$] (δ 91.0 ppm) [11] and [WFe_2(μ_3-CC_6H_4Me-4)(μ-Me_3Si*C*≡*C*$SiMe_3$)(μ-CO)$(CO)_6$(η-C_5H_5)] (δ 75.7 and 107.8 ppm) [12]. The observation of a single ^{13}C $\{^1H\}$ NMR resonance for the R*C*≡*C*R (R = C_6H_4Me-4) carbon atoms, and correspondingly a single Me-4 resonance in both the ^{13}C $\{^1H\}$ and ^1H NMR spectra, requires a symmetric structure of the type shown, in which the μ-RC≡CR ligand (R = C_6H_4Me-4) transversely bridges a cobalt–cobalt bond. Further experiments revealed that X could be more rationally prepared by treating either Ic or II with a further equivalent of [ReCr(≡CC_6H_4Me-4)$(CO)_9$] (Scheme 2). It should be noted that formation of an alkyne RC≡CR via coupling of two CR groups is a well established process in cluster chemistry [13–15].

As noted above, thermolysis of Ic was expected to give only II, but we now find that small amounts (ca. 5–10%) of a purple complex XI are also formed (Scheme 2). Spectroscopic data for XI are in most respects very similar to those of II, but there are significant differences in the aromatic regions of the ^1H and ^{13}C $\{^1H\}$ NMR spectra. In particular the multiplet associated with the C_6H_4Me-4 protons in XI occurs at unusually high field (ca. δ 5.56 ppm), and the C_6H_4Me-4 carbons atoms show a similar shielding in the ^{13}C $\{^1H\}$ NMR spectrum (δ range 88.4–125.7 ppm). These values are typical of those for metal bound π-arene ligands. It therefore seems likely that thermolysis of Ic can either result in elimination of a $Cr(CO)_x$ fragment to give II or in migration of a $Cr(CO)_3$ fragment to the C_6H_4Me-4 ring to give the π-arene derivative XI.

Experimental

Solvents were rigourously dried and degassed before use, and all reactions were carried out in Schlenk tubes, under oxygen-free nitrogen. Light petroleum refers to the fraction of b.p. 40–60 °C. Alumina used for chromatography columns (20 × 2 cm) was B.D.H. aluminium oxide (Brockman activity II), alternatively Florisil was used (Aldrich 100–200 mesh). Infrared spectra were recorded with a Nicolet 10-MX FT spectrophotometer, and all NMR spectra were recorded with JNM FX90Q, FX200 or GX400 instruments. The complexes I and II were prepared by previously described methods [1] but additional by-products were obtained as noted in the next.

Reaction of $[WReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{15}]$ (Ia) with PMe_2Ph

(i) A solution of Ia (0.22 g, 0.20 mmol) in Et_2O (100 cm^3) was treated with one equivalent of PMe_2Ph (0.03 g, 0.20 mmol) and the mixture was stirred for ca. 40 min. Solvent was removed in vacuo and the residue was dissolved in dichloromethane (10 cm^3). Alumina (5 g) was added and solvent was again removed in vacuo. The dry alumina with the adsorbed product was transferred to the top of an alumina column. Elution with CH_2Cl_2/light petroleum (1/10) gave a green fraction containing III, and then a second green fraction containing IV. Removal of solvent in vacuo and recrystallisation from CH_2Cl_2/light petroleum gave dark green $[WReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{14}(PMe_2Ph)]$ (III) (0.02 g, 10%) and green crystals of $[WReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{13}(PMe_2Ph)_2]$ (IV) (ca. 30%).

(ii) Compound IV was prepared in good yield by treating Ia (0.26 g, 0.26 mmol) in Et_2O (20 cm^3) with two equivalents of PMe_2Ph (0.07 g, 0.52 mmol). After 2 h the solvent was removed in vacuo and the residue was dissolved in the minimum volume of CH_2Cl_2/light petroleum (2/5) and chromatographed on an alumina column. Elution with the same solvent afforded a green band which was collected. Removal of solvent in vacuo and recrystallisation from CH_2Cl_2/light petroleum gave dark green microcrystals of $[WReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{13}(PMe_2Ph)_2]$ (IV) (0.22 g, 70%).

Reaction of $[WReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{15}]$ (Ia) with $Ph_2PCH_2PPh_2$

A solution of Ia (0.18 g, 0.18 mmol) in Et_2O (20 cm^3) was stirred for ca. 40 min with one equivalent of $Ph_2PCH_2PPh_2$ (0.07 g, 0.18 mmol). Solvent was removed in vacuo and work-up as described above for IV gave green microcrystals of $[WReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{13}(Ph_2PCH_2PPh_2)]$ (V) (0.19 g, 80%).

Reaction of $[WReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{15}]$ (Ia) with PPh_2H

A solution of Ia (0.41 g, 0.40 mmol) in Et_2O (40 cm^3) was stirred for 1 h with two equivalents of PPh_2H (0.15 g, 0.80 mmol). Work-up as described for IV gave green microcrystals of $[WCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}PPh_2)(CO)_8(PPh_2H)]$ (VI) (0.24 g, 60%).

Reaction of $[ReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{10}]$ (II) with $Ph_2PCH_2PPh_2$

(i) A solution of II (0.29 g, 0.42 mmol) in Et_2O (15 cm^3) was stirred for 1 h with one equivalent of $Ph_2PCH_2PPh_2$ (0.16 g, 0.42 mmol). Solvent was removed in vacuo and the residue was dissolved in the minimum of CH_2Cl_2/light petroleum (1/4) and chromatographed on an alumina column. Elution with the same solvent afforded a small amount of unchanged II, followed by a dark grey band which was collected. Solvent was removed in vacuo and recrystallisation from CH_2Cl_2/light petroleum gave black crystals of $[ReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(Ph_2PCH_2PPh_2)]$ (VII) (0.27 g, 63%).

(ii) A solution of VII (0.27 g, 0.26 mmol) in Et_2O (5 cm^3) was stirred for 48 h with a second equivalent of $Ph_2PCH_2PPh_2$ (0.10 g, 0.26 mmol). The solution became paler and a black precipitate formed. Solvent was removed in vacuo and the precipitate was washed with Et_2O (3×2 cm^3) to remove traces of unreacted VII. Recrystallisation from CH_2Cl_2/light petroleum gave dark green crystals of $[ReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_7(Ph_2PCH_2PPh_2)_2]$ (VIII) (0.23 g, 65%).

(iii) A solution of VIII (0.10 g, 0.07 mmol) in tetrahydrofuran (6 cm^3) was refluxed, for 2 h, during which the solution changed from green to orange. Solvent was removed in vacuo and the orange solid was chromatographed on an alumina column. The orange band was collected and solvent removed in vacuo. Crystallisation from CH_2Cl_2/light petroleum gave orange microcrystals of $[ReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(Ph_2PCH_2PPh_2)]$ (IX) (0.06 g, 60%). It was found that VIII also rearranged to orange IX when its solutions in THF were passed down an alumina column.

Reaction of $[ReCr(\equiv CC_6H_4Me\text{-}4)(CO)_9]$ with $[Co_2(CO)_8]$

A light petroleum (6 cm^3) solution of $[ReCr(\equiv CC_6H_4Me\text{-}4)(CO)_9]$ (0.58 g, 0.97 mmol) and $[Co_2(CO)_8]$ (0.33 g, 0.97 mmol) was stirred at room temperature for 3 h then the mixture was chromatographed on a Florisil column (20×2 cm). Elution with light petroleum/CH_2Cl_2 (19/1) gave a brown eluate of X, followed by a green eluate of Ic, which was identified by IR spectroscopy [1]. Solvent was removed from the brown fraction in vacuo, and crystallisation from hexane afforded brown crystals of $[Re_2Co_2\{\mu\text{-}(RCCR)\}(CO)_{12}]$ (X) (0.38 g, 38%).

Thermolysis of $[CrReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{15}]$ (Ic)

A toluene (10 cm^3) solution of $[CrReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{15}]$ (Ic) (0.47 g, 0.53 mmol) was refluxed for ca. 10 min. The solvent was removed in vacuo, and the residue was dissolved in light petroleum (ca. 5 cm^3) and chromatographed on a Florisil column (2×20 cm). Elution with light petroleum gave a major brown band, which was identified as II by IR spectroscopy [1]. A second purple band was also collected and solvent was removed in vacuo. Recrystallisation of the purple residue from CH_2Cl_2/light petroleum gave dark purple crystals of $[CrReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{13}]$ (XI) (0.04 g, 9%).

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References

1 J.C. Jeffery, D.B. Lewis, G.E. Lewis, and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1985) 2001.
2 D.G. Evans, J.A.K. Howard, J.C. Jeffery, D.B. Lewis, G.E. Lewis, M.J. Grosse-Ophoff, M.J. Parrott, and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1986) 1723.
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 L. Busetto, J.C. Jeffery, R.M. Mills, F.G.A. Stone, M.J. Went, and P. Woodward, J. Chem. Soc., Dalton Trans., (1983) 101.

5 P.G. Byrne, M.E. Garcia, W.H. Tran-Huy, J.C. Jeffery, and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1987) 1243.

6 J.C. Jeffery and J.G. Lawrence-Smith, J. Organomet. Chem., 280 (1985) C34.

7 P. Dunn, J.C. Jeffery, and P. Sherwood, J. Organomet. Chem., 311 (1986) C55.

8 J.C. Jeffery and J.G. Lawrence-Smith, J. Chem. Soc., Chem. Commun., (1985) 275; ibid., (1986) 17.

9 A.J. Downard, B.H. Robinson, and J. Simpson, Organometallics, 5 (1986) 1122.

10 S. Aime, M. Botta, R. Gobetto, and D. Osella, J. Organomet. Chem., 320 (1987) 229.

11 S. Aime, L. Milone, R. Rosetti, and P.L. Stanghellini, Inorg. Chim. Acta, 22 (1977) 135.

12 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.

13 E. Delgado, J.C. Jeffery, and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1986) 2105 and references therein.

14 J.R. Shapley, J-T. Park, M.R. Churchill, C. Bueno, and H.J. Wasserman, J. Am. Chem. Soc., 103 (1981) 7385; M.R. Churchill, C. Bueno, and H.J. Wasserman, Inorg. Chem., 21 (1982) 640.

15 D. Nuel, F. Dahan, and R. Mathieu, Organometallics, 4 (1985) 1436.