

Preliminary communication

SYNTHESIS AND REACTIONS OF PHOSPHIDO-BRIDGED μ_3 -ALKYLIDYNE CLUSTERS; X-RAY CRYSTAL STRUCTURES OF THE COMPLEXES $[\text{Co}_2\text{W}(\mu\text{-PEt}_2)_3(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$, $[\text{Co}_2\text{W}\{\mu_3\text{-C(R)C(Et)C(Et)C(O)}\}(\mu\text{-CO})(\text{CO})_4(\text{PPh}_2\{\text{C(Et)=CHEt}\})(\eta\text{-C}_5\text{H}_5)]$, AND $[\text{CoW}\{\mu\text{-C(R)C(Et)C(Et)C(OH)}\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)]$ ($\text{R} = \text{C}_6\text{H}_4\text{Me-4}$)

PAUL DUNN, JOHN C. JEFFERY * and PAUL SHERWOOD

Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS (Great Britain)

(Received June 4th, 1986)

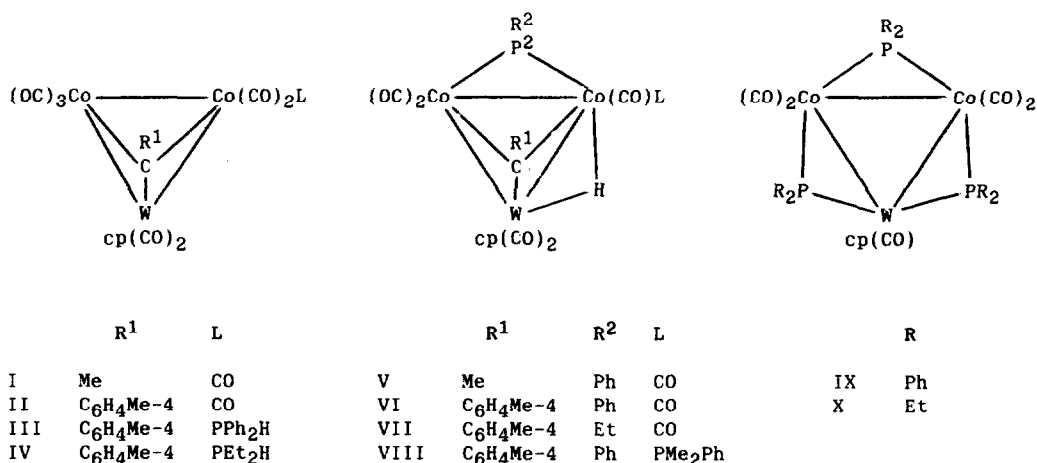
Summary

Reactions of the phosphido-bridged complexes $[\text{Co}_2\text{W}(\mu\text{-H})(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\mu\text{-PR}_2)(\text{CO})_6(\eta\text{-C}_5\text{H}_5)]$ ($\text{R} = \text{Ph}$ or Et) with PR_2H ($\text{R} = \text{Ph}$ or Et) or $\text{RC}\equiv\text{CR}$ ($\text{R} = \text{Me}$ or Et) are dominated by processes involving facile P–C, C–C and C–H bond formation. The X-ray structures of the complexes $[\text{Co}_2\text{W}(\mu\text{-PEt}_2)_3(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$, $[\text{Co}_2\text{W}\{\mu_3\text{-C(R)C(Et)C(Et)C(O)}\}(\mu\text{-CO})(\text{CO})_4(\text{PPh}_2\{\text{C(Et)=CHEt}\})(\eta\text{-C}_5\text{H}_5)]$, and $[\text{CoW}\{\mu\text{-C(R)C(Et)C(Et)C(OH)}\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)]$ ($\text{R} = \text{C}_6\text{H}_4\text{Me-4}$) have been determined.

Currently there is interest in the possibility that mixed-metal clusters may exhibit novel bi-metallic reactivity patterns [1]. In this context we have recently reported that the coordinatively unsaturated complexes $[\text{Fe}_2\text{W}(\mu\text{-H})(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\mu\text{-PR}^1_2)(\text{CO})_6(\eta\text{-C}_5\text{H}_5)]$ ($\text{R}^1 = \text{Ph}$ or Et) react with alkynes ($\text{R}^2\text{C}\equiv\text{CR}^2$, $\text{R}^2 = \text{Me}$, Et or Ph) to give the compounds $[\text{Fe}_2\text{W}(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})\{\mu\text{-C(O)C(R}^2\text{)CHR}^2\}(\mu\text{-PR}^1_2)(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$, a process which involves conversion of an alkyne to a μ_2 -vinylacyl moiety [2]. Herein we report the coupling of alkyne, alkylidyne and carbonyl ligands at a closely related Co_2W heterotrimetal centre.

Treatment of I with one equivalent of PPh_2H gives V [3]. We now find that the related reactions between PR_2H ($\text{R} = \text{Ph}$ or Et) and the tolylmethylidyne complex II afford good yields (60–70%) of the terminal PR_2H compounds III and IV [4], which rearrange (CH_2Cl_2 , 40°C , ca. 1–2 h) to give the phosphido-bridged derivatives VI and VII [5].

The $\mu\text{-PR}_2$ groups in $[\text{Fe}_2\text{W}(\mu\text{-H})(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\mu\text{-PR}_2)(\text{CO})_7(\eta\text{-C}_5\text{H}_5)]$ ($\text{R} = \text{Et}$ or Ph) exert an important labilising effect on the carbonyl ligands [2]. A similar effect is evident for the Co_2W complexes VI and VII. Thus treatment of VI with one equivalent of PMe_2Ph (Et_2O , 20°C , 1 h) affords VIII (55%), [6], whilst excess



PPh₂H (CH₂Cl₂, 40°C, 2 h) predominantly (ca. 45%) gives the tris-phosphido bridged complex IX [7], together with free PPh₂(CH₂C₆H₄Me-4) and minor (< 10%) byproducts such as XI [8] which contain coordinated PPh₂(CH₂C₆H₄Me-4) ligands. The related reaction of VII with excess PEt₂H gave X (50%). An X-ray study on X [9] (Fig. 1) shows that the edges of the Co₂W triangle of metal atoms are asymmetrically bridged by μ -PEt₂ ligands, a situation comparable with that found in the homonuclear trirhodium complex [Rh₃(μ -PPh₂)₃(CO)₅] [10]. The unexpected absence of a μ_3 -CC₆H₄Me-4 group in IX is evidently linked with the formation of PPh₂(CH₂C₆H₄Me-4). Reductive elimination of the μ_3 -CC₆H₄Me-4 group might involve transfer of two hydrogen atoms to the μ_3 -C carbon to form an alkyl (CH₂C₆H₄Me-4) which migrates to the phosphorus atom of a μ -PPh₂ group.

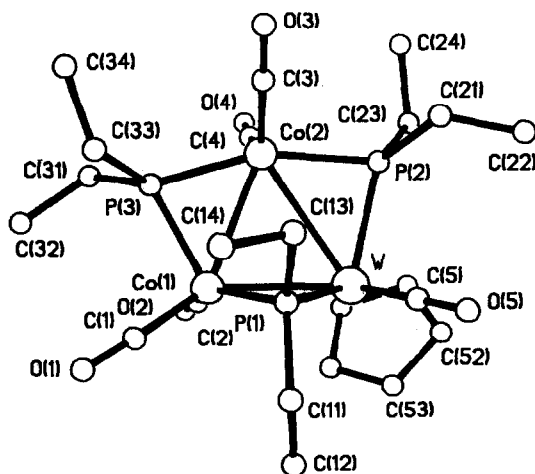


Fig. 1. The molecular structure of $[\text{Co}_2\text{W}(\mu\text{-PEt}_2)_3(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ (X). W-Co(1) 2.684(1), W-Co(2) 2.995(1), Co(1)-Co(2) 2.712(1), W-P(1) 2.410(2), W-P(2) 2.378(1), Co(1)-P(1) 2.150(1), Co(1)-P(3) 2.170(1), Co(2)-P(2) 2.189(1), Co(2)-P(3) 2.131(1) Å, Co(1)-W-Co(2) 56.7(1), W-Co(1)-Co(2) 67.4(1), W-Co(2)-Co(1) 55.8(1), W-P(1)-Co(1) 71.9(1), W-P(2)-Co(2) 81.9(1), Co(1)-P(3)-Co(2) 78.2(1)°.

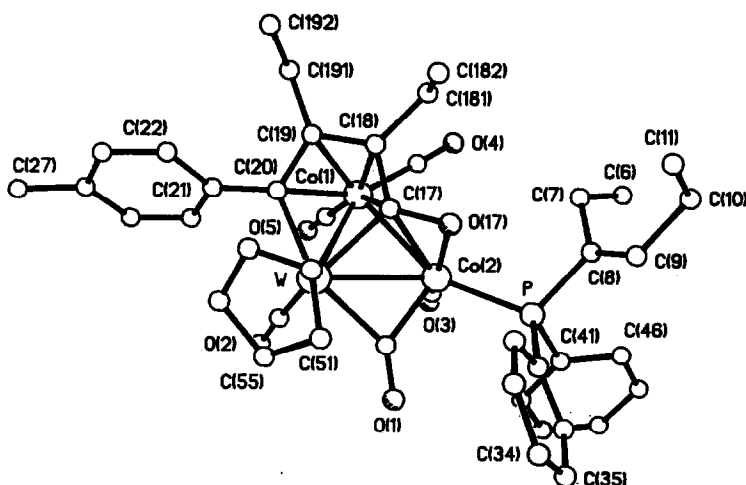
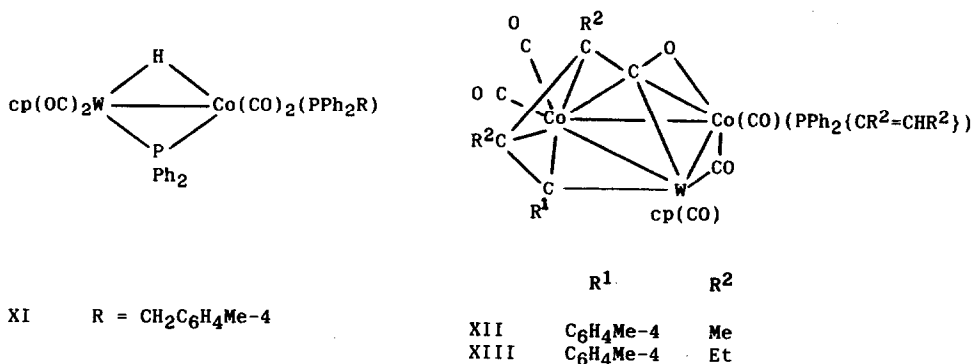


Fig. 2. The molecular structure of $[\text{Co}_2\text{W}\{\mu_3\text{-C}(\text{C}_6\text{H}_4\text{Me-4})\text{C}(\text{Et})\text{C}(\text{Et})\text{C}(\text{O})\}(\mu\text{-CO})(\text{CO})_4\text{-}(\text{PPh}_2\{\text{C}(\text{Et})=\text{CHEt}\})(\eta\text{-C}_5\text{H}_5)]$ (XIII). W–Co(1) 2.809(1), W–Co(2) 2.784(1), Co(1)–Co(2) 2.668(1), W–C(17) 2.142(7), W–C(20) 2.197(7), Co(1)–C(17) 2.221(7), Co(1)–C(18) 2.092(8), Co(1)–C(19) 2.100(8), Co(1)–C(20) 2.077(7), Co(2)–C(17) 2.132(8), Co(2)–O(17) 1.935(5), C(17)–O(17) 1.321(8) Å.

Displacement of the resulting bulky tertiary phosphine $\text{PPh}_2(\text{CH}_2\text{C}_6\text{H}_4\text{Me-4})$ by excess PPh_2H could then provide a route to IX. Similar alkyl intermediates may be involved in the formation of $[\text{Fe}_2\text{W}(\mu_3\text{-OCCH}_2\text{C}_6\text{H}_4\text{Me-4})(\mu\text{-PPh}_2)_2(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ from $[\text{Fe}_2\text{W}(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\mu\text{-CO})(\text{CO})_8(\eta\text{-C}_5\text{H}_5)]$ and excess PPh_2H [11], but here alkyl migration to CO evidently takes precedence over P–C bond formation.

Compound VI also reacts (CH_2Cl_2 , 40°C , 12 h) with excess $\text{RC}\equiv\text{CR}$ ($\text{R} = \text{Me}$ or Et) to give the bis-alkyne derivatives XII and XIII [12] in ca. 50% yields. The X-ray structure of the hex-3-yne complex XIII [9] (Fig. 2) reveals that one molecule of the alkyne has been stereospecifically converted to a *cis*-vinyl group which is attached to phosphorus. A second alkyne has coupled with the $\mu_3\text{-CC}_6\text{H}_4\text{Me-4}$ group and a CO ligand affording a novel $\mu_3\text{-C}(\text{C}_6\text{H}_4\text{Me-4})\text{C}(\text{Et})\text{C}(\text{Et})\text{C}(\text{O})$ group which is σ -bound to tungsten via C(17) and C(20) with η^4 and η^2 attachments to Co(1) and Co(2) respectively.

Treatment of XII or XIII with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ or Me_3OBF_4 leads to immediate cluster fragmentation and good yields (ca. 65%) of the neutral hydroxy and methoxy



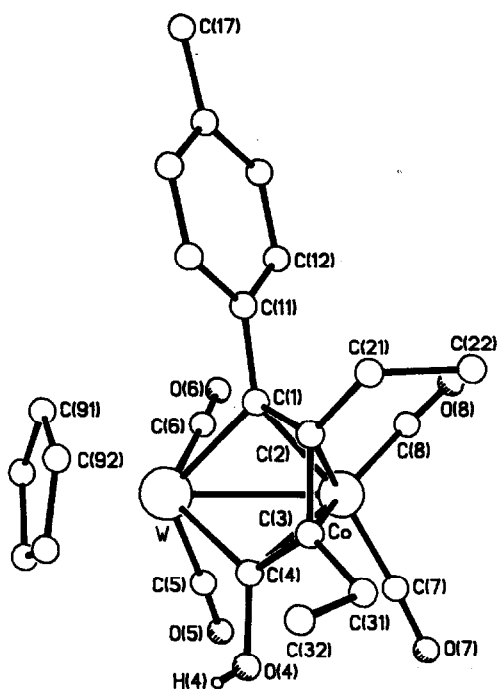
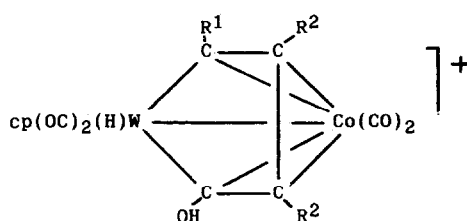
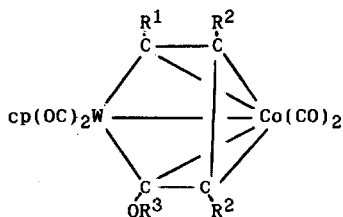


Fig. 3. The molecular structure of $[\text{CoW}\{\mu\text{-C}(\text{C}_6\text{H}_4\text{Me-4})\text{C}(\text{Et})\text{C}(\text{Et})\text{C}(\text{OH})\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)]$ (XV). W-Co 2.702(1), W-C(1) 2.197(4), W-C(4) 2.134(4), Co-C(1) 2.056(4), Co-C(2) 2.132(4), Co-C(3) 2.135(4), Co-C(4) 2.099(4), C(4)-O(4) 1.378(5) Å.

Co-W dimetal complexes XIV–XVI [13] are obtained. The structure of the hydroxy derivative XV [9] (Fig. 3) shows that the Co–W bond is bridged by a $\mu\text{-C}(\text{C}_6\text{H}_4\text{Me-4})\text{C}(\text{Et})\text{C}(\text{Et})\text{C}(\text{OH})$ group in a manner which resembles that found in homonuclear di-iron “ferrole” complexes such as $[\text{Fe}_2\{\mu\text{-C}(\text{OH})\text{C}(\text{Et})\text{C}(\text{Et})\text{C}(\text{OH})\}(\text{CO})_6]$ [14]. In the presence of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (XV) reversibly protonates at tungsten affording the cationic hydrido complex XVII [15].

The reactions of VI or VII described above involve facile P–C bond formation, a feature not yet observed for closely related Fe_2W clusters such as $[\text{Fe}_2\text{W}(\mu\text{-H})(\mu_3\text{-$



	R ¹	R ²	R ³
XIV	C ₆ H ₄ Me-4	Me	H
XV	C ₆ H ₄ Me-4	Et	H
XVI	C ₆ H ₄ Me-4	Et	Me

	R ¹	R ²
XVII	C ₆ H ₄ Me-4	Et

$\text{CC}_6\text{H}_4\text{Me-4}(\mu\text{-PR}_2)(\text{CO})_6(\eta\text{-C}_5\text{H}_5)]$ ($\text{R} = \text{Et}$ or Ph). This may reflect bimetallic reactivity effects. Alternatively regioselective control of the reaction pathway may be important. Thus, generation of key alkyl or vinyl intermediates in the Fe_2W system, in which a heteronuclear Fe-W bond is bridged by phosphorus, could occur at the Fe atom remote from phosphorus thereby avoiding P-C bond formation.

References and Notes

- 1 A.J. Carty, P.H. Dixneuf, R. Regragui, and N.J. Taylor, *Organometallics*, **5** (1986) 1, and ref. therein.
- 2 J.C. Jeffery and J.G. Lawrence-Smith, *J. Chem. Soc., Chem. Commun.*, (1986) 17.
- 3 J.C. Jeffery and J.G. Lawrence-Smith, *J. Organomet. Chem.*, **280** (1985) C34.
- 4 For Compound III, $\nu_{\text{max}}(\text{CO})$ at 2047 m, 2000 s, 1985 s, 1910 wbr, and 1851 wbr cm^{-1} (CH_2Cl_2). NMR (CD_2Cl_2): ^1H , δ 5.57 ppm (d, PPh_2H , $J(\text{PH})$ 357 Hz); $^{31}\text{P}\{-^1\text{H}\}$, δ 30.1 ppm (s, PPh_2H).
- 5 For Compound VI, $\nu_{\text{max}}(\text{CO})$ at 2040 m, 2014 s, 1984 s, 1958 w, and 1875 wbr cm^{-1} (methylcyclohexane). NMR (CD_2Cl_2): ^1H , δ -13.92 ppm (d, $\mu\text{-H}$, $J(\text{PH})$ 23, $J(\text{WH})$ 35 Hz); $^{31}\text{P}\{-^1\text{H}\}$, δ 232.9 ppm (br, s, $\mu\text{-PPh}_2$); $^{13}\text{C}\{-^1\text{H}\}$, δ 241.2 ppm (d, $\mu_3\text{-C}$, $J(\text{PC})$ 25 Hz).
- 6 For Compound VIII, $\nu_{\text{max}}(\text{CO})$ at 2011 s, 1966 s, 1940 m, 1935 sh, and 1878 wbr cm^{-1} (methylcyclohexane). NMR (CD_2Cl_2): ^1H , δ -14.61 ppm (dd, $\mu\text{-H}$, $J(\text{PH})$ 27, 27, $J(\text{WH})$ 47 Hz); $^{31}\text{P}\{-^1\text{H}\}$, δ 218.1 (br, s, $\mu\text{-P}$), and 12.6 ppm (br, s, PMe_2Ph); $^{13}\text{C}\{-^1\text{H}\}$, δ 235.4 ppm (s, $\mu_3\text{-C}$).
- 7 For Compound IX, $\nu_{\text{max}}(\text{CO})$ at 2011 m, 1975 s, 1967 s, 1916 m, and 1864 w cm^{-1} (methylcyclohexane). NMR (CD_2Cl_2): $^{31}\text{P}\{-^1\text{H}\}$ at 20°C , δ 289.4 (br, s, $\text{Co}_2(\mu\text{-P})$), and 155.5 ppm (br, s, $\text{CoW}(\mu\text{-P})$); $^{31}\text{P}\{-^1\text{H}\}$ at -40°C , δ 289.5 (br, s, $\text{Co}_2(\mu\text{-P})$), and 166.3, 143.8 ppm (br, $2\times$, $\text{CoW}(\mu\text{-P})$).
- 8 For Compound XI, $\nu_{\text{max}}(\text{CO})$ at 1979 w, 1930 s, 1905 sh, and 1850 m cm^{-1} (CH_2Cl_2). NMR (CD_2Cl_2): ^1H , δ -11.94 (dd, $\mu\text{-H}$, $J(\text{PH})$ 32, 46 Hz), and 4.09 ppm (d, $\text{CH}_2\text{C}_6\text{H}_4\text{Me-4}$, $J(\text{PH})$ 11 Hz); $^{31}\text{P}\{-^1\text{H}\}$, δ 170.5 (d, $\mu\text{-P}$, $J(\text{PP})$ 73 Hz), and 67.9 ppm (d, $\text{PPh}_2(\text{CH}_2\text{C}_6\text{H}_4\text{Me-4})$, $J(\text{PP})$ 73 Hz). The structure of XI has been confirmed by an X-ray study which will be reported at a later date in a full paper.
- 9 Crystal data. For X: $\text{C}_{22}\text{H}_{35}\text{Co}_2\text{O}_5\text{P}_3\text{W}$, $M = 774.1$, monoclinic, space group $P2_1/n$, a 9.698(2), b 28.332(6), c 10.682(4) Å, β 76.72(2)°, U 2857(1) Å³, $Z = 4$, D_x 1.80 g cm^{-3} , $F(000) = 1520$, $\mu(\text{Mo-K}_\alpha)$ 54.46 cm^{-1} . Current $R = 0.030$ ($R_w = 0.032$) for 4441 absorption corrected intensities (22°C , ω -2 θ scans, $2\theta \leq 50^\circ$, $I \geq 2.5\sigma(I)$). For XIII: $\text{C}_{43}\text{H}_{43}\text{Co}_2\text{O}_6\text{PW}$, $M = 988.5$, monoclinic, space group $P2_1/a$ (non-standard setting of $P2_1/c$), a 18.54(1), b 9.572(5), c 22.81(2) Å, β 97.95(6)°, U 4010(5) Å³, $Z = 4$, D_x 1.64 g cm^{-3} , $F(000) = 1968$, $\mu(\text{Mo-K}_\alpha)$ 38.25 cm^{-1} . Current $R = 0.040$ ($R_w = 0.039$) for 4614 absorption corrected intensities (20°C , ω -scans, $2\theta \leq 50^\circ$, $I \geq 2.5\sigma(I)$). For XV: $\text{C}_{24}\text{H}_{23}\text{CoO}_5\text{W}$, $M = 634.2$, triclinic, space group $P\bar{1}$, a 8.616(2), b 9.610(2), c 13.747(3) Å, α 89.31(2), β 95.41(2), γ 87.36(2)°, U 1131.8(4) Å³, $Z = 2$, D_x 1.86 g cm^{-3} , $F(000) = 616$, $\mu(\text{Mo-K}_\alpha)$ 59.51 cm^{-1} . Current $R = 0.026$ ($R_w = 0.026$) for 3780 absorption corrected intensities (20°C , ω -2 θ scans, $2\theta \leq 50^\circ$, $I \geq 2.5\sigma(I)$). Nicolet P2₁ or P3 diffractometers, Mo-K α X-radiation (λ 0.71069 Å). The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by the full literature citation for this communication.
- 10 R.B. English, R.J. Haines, and N.D.C.T. Steen, *J. Organomet. Chem.*, **209** (1981) C34.
- 11 J.C. Jeffery and J.G. Lawrence-Smith, *J. Chem. Soc., Chem. Commun.*, (1985) 275.
- 12 For Compound XIII, $\nu_{\text{max}}(\text{CO})$ at 2021 s, 1970 m, 1937 w, and 1760 m cm^{-1} (CH_2Cl_2). NMR (CD_2Cl_2): ^1H , δ 6.12 ppm (dt, $\text{C}(\text{Et})=\text{CH}(\text{Et})$, $J(\text{PH})$ 22, $J(\text{HH})$ 7 Hz); $^{31}\text{P}\{-^1\text{H}\}$, δ 66.5 ppm (s, PPh_2R); $^{13}\text{C}\{-^1\text{H}\}$, δ 243.5 (s, $\mu\text{-CO}$, $J(\text{WC})$ 74 Hz), 227.4 (s, WCO , $J(\text{WC})$ 140 Hz), 212.9, 209.5, 202.3 ($3\times$, CoCO), 190.0 (s, $\text{C}(\text{R})\text{C}(\text{Et})\text{C}(\text{Et})\text{C}(\text{O})$, $J(\text{WC})$ 54 Hz), 157.9, 150.1, 132.9 ($3\times$, $\text{C}(\text{R})\text{C}(\text{Et})\text{C}(\text{Et})\text{C}(\text{O})$), 151.0 (d, $\text{C}(\text{Et})=\text{CH}(\text{Et})$, $J(\text{PC})$ 20 Hz), and 112.6 ppm (s, $\text{C}(\text{Et})=\text{CH}(\text{Et})$).
- 13 For Compound XV, $\nu_{\text{max}}(\text{CO})$ at 2016 s, 1956 m, and 1891 m cm^{-1} (CH_2Cl_2). NMR (CD_2Cl_2): ^1H , δ 4.84 ppm (br, s, OH); $^{13}\text{C}\{-^1\text{H}\}$, δ 228.9 (s, WCO , $J(\text{WC})$ 144 Hz), 224.6 (s, WCO), 205.4 (s, $\text{Co}(\text{CO})_2$), 177.3 (s, COH), and 149.5, 145.6, 137.5 ppm ($3\times$, $\text{C}(\text{R})\text{C}(\text{Et})\text{C}(\text{Et})$).
- 14 S. Aime, L. Milonc, E. Sappa, A. Tiripicchio, and A.M.M. Longredi, *J. Chem. Soc., Dalton Trans.*, (1979) 1664.
- 15 For Compound XVII, $\nu_{\text{max}}(\text{CO})$ at 2079 s, 2061 m, and 2027 s cm^{-1} (CH_2Cl_2). NMR (CD_2Cl_2): ^1H , δ -3.85 (s, WH), and 7.65 ppm (br, s, OH); $^{13}\text{C}\{-^1\text{H}\}$, δ 199.5, 198.7 ($2\times$, $\text{Co}(\text{CO})_2$), 196.4, 195.1 ($2\times$, $\text{W}(\text{CO})_2$), 178.3 (s, COH), and 144.9, 141.8, 133.3 ppm ($3\times$, $\text{C}(\text{R})\text{C}(\text{Et})\text{C}(\text{Et})$).