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Ring Opening or Redox Reactions on Treating $[M(CO)_3(Ph_2PCH_2PPh_2\text{-}PP')(Ph_2PCH_2PPh_2\text{-}P)]$ (M = Cr, Mo or W) with Cu(I), Ag(I), Au(I) or Hg(II) Complexes: Crystal Structure of $[(OC)_2W(\mu\text{-}Ph_2PCH_2PPh)_2(\mu\text{-}Cl)(\mu\text{-}CO)Cu]$

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We have shown that $Ph_2PCH_2PPh_2$ (dppm) complexes of the types *fac*-$[M^1(CO)_3(\text{dppm-PP}')(\text{dppm-P})]$ (M^1 = Mo or W) or *mer*-$[M^1(CO)_3(\text{dppm-PP}')(\text{dppm-P})]$ (M^1 = Cr, Mo or W) react with labile rhodium(I) or iridium(I) complexes to give heterobimetallics containing *trans,trans*-$[M^1(\mu\text{-dppm})_2M^2]$ (M^2 = Rh or Ir) moieties in high yield [1]. We now wish to report that similar treatment of *fac*- or *mer*-$[M^1(CO)_3(\text{dppm-PP}')(\text{dppm-P})]$ with Cu(I), Ag(I), Au(I) or Hg(II) compounds sometimes induces ring-opening to give heterobimetallics but in other cases rapid REDOX reactions, or more complicated processes, occur.

Treatment of *mer*-$[M^1(CO)_3(\text{dppm-PP}')(\text{dppm-P})]$ with CuI or CuCl in dichloromethane at 20 °C gives heterobimetallics of composition $[M^1Cu(CO)_3X(\text{dppm})_2]$ (X = Cl or I) which are red (M^1 = Cr) or orange (M^1 = Mo or W), in yield of 50–65%: similar treatment of *fac*-isomers gives mixtures**. The complexes are non-conducting and the IR spectra show a low-frequency band (≦1810 cm^{-1}) in the carbonyl region suggesting a bridging carbonyl might be present, *e.g.* for M^1 = W, X = Cl, ν(CO) = 1784, 1838 and 1952 cm^{-1} (CH_2Cl_2 solution). In the $^1H\text{-}\{^{31}P\}$ spectra all show an AB pattern at 20 °C for the PCH_2P protons indicative of a rigid system with pseudo-equatorial and pseudo-axial hydrogens. The $^{31}P\text{-}\{^1H\}$ NMR spectra are all temperature dependent, the spectra for the W-CuCl complex are shown in Fig. 1. For the P-nuclei bound to W the pattern is of the AA′XX′ type with eight of the ten lines possible being observed (the outer lines of the ab subspectrum corresponding to '(K)' being too low in intensity to observe) [2]. For the P-nuclei bound to copper the resonance is broad at 20 °C but sharpens up when the temperature is lowered and is of the AA′-XX′ type below −60 °C. Since all six compounds $[M^1Cu(CO)_3X(\text{dppm})_2]$ exhibit a similar behaviour over the temperature range +20 °C to −60 °C and the equatorial and axial hydrogens of the CH_2 give distinct resonance at +20 °C we ascribe the broadening to quadrupole effects (both copper isotopes have $I = 3/2$) and not to chemical exchange. The crystal structure of the W–CuCl complex has been determined and is shown in Fig. 2. Some features of

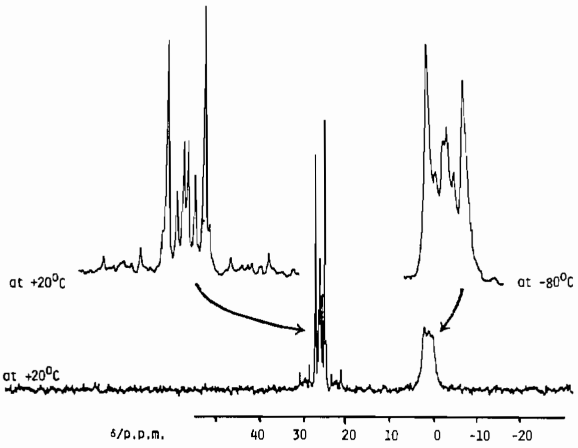

Fig. 1. $^{31}P\text{-}\{^1H\}$ NMR spectra of $[(OC)_3W(\mu\text{-dppm})_2CuCl]$, in CH_2Cl_2 at 40.25 MHz, showing the effect of temperature on the P_X resonances. The spectrum at −80 °C is virtually the same as at −60 °C, δ_{P_A} = 26.2 p.p.m., $^1J(WP_A)$ = 301 Hz, δP_X = 0.7 p.p.m., |N| = 88 Hz, |L| = 70 Hz, |M| = 34 Hz.

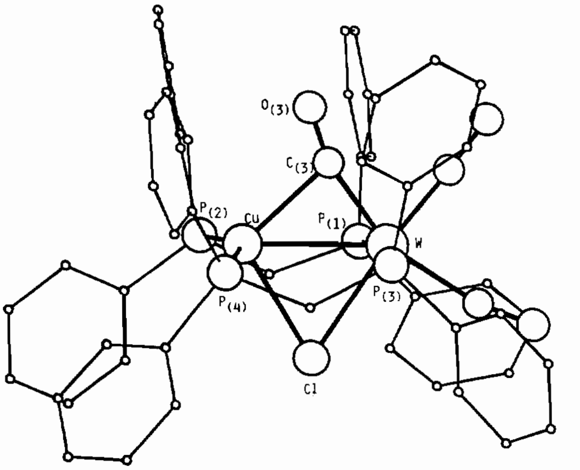

Fig. 2. Molecular structure of $[(OC)_2W(\mu\text{-}Ph_2PCH_2PPh_2)_2(\mu\text{-}Cl)(\mu\text{-}CO)Cu]$. Selected bond lengths: W–Cu 275.9(4), W–C(3) 200.4(11), Cu–C(3) 226.7(8), W–Cl 259.2(5), Cu–Cl 255.3(5) pm. Selected bond angles: P(1)–W–P(3) 167.3(1), P(2)–Cu–P(4) (internal) 211.5(1), W–C(3)–Cu 80.2, W–Cl–Cu 64.8°.

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**Crystal data: Orange solvent dependent plates, $CuC_{54}Cl_3H_{46}O_3P_4W$, M = 1220.7, Monoclinic, Space group $P2_1/c$ (no. 14), a = 1076.0(2), b = 2513.2(4), c = 2067.5(3) pm, β = 112.62(1)°, U = 5.161 nm^3, D_c = 1.57 g cm^{-3}, Z = 4, Mo-K_α radiation, λ = 71.069 pm, μ(Mo-K_α) = 27.7 cm^{-1}, 4° < 2σ < 45°. Final R value 0.0359 (unit weights) for 6138 unique reflections [$I > 2(I)$].

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interest are (i) the presence of both Cl and CO bridges and (ii) the remarkably high P(2)–Cu–P(4) internal angle of 211.5(1)° whereas the internal angle P(1)–W–P(2) is 167.3(1)°. Many crystal structures containing $M^1(\mu\text{-dppm})_2M^2$ moieties have been determined and usually the internal angle P–M–P is less than 190°. Two very interesting isomeric forms of $[\eta^5\text{-}C_5H_5W(CO)_3Cu(PPh_3)_2]$ have been described and one of them shows semi-bridging CO's and a W–Cu bond with a very similarly internuclear distance {277.1(1) pm} to ours [3].

In contrast to the behaviour of Cu(I), we find that Hg(II) generally, oxidizes the $[M^1(CO)_3(\text{dppm-PP}')(\text{dppm-P})]$ to a mononuclear M^1(II) complex. Thus treatment of *fac*- or *mer*-$[Mo(CO)_3(\text{dppm-PP}')(\text{dppm-P})]$ with $HgCl_2$ in CH_2Cl_2 at 20 °C gives $[Mo(CO)_2(\text{dppm-PP}')_2Cl]Cl$ in good (>60%) yield, together with metallic mercury: we have prepared this complex by treating *cis*-$[Mo(CO)_2(\text{dppm-PP}')_2]$ with Cl_2. The corresponding bromide and iodide $[Mo(CO)_2(\text{dppm-PP}')_2X]X$ (X = Br or I) have been prepared previously by treating *cis*-$[Mo(CO)_2(\text{dppm-PP})_2]$ with X_2 [4]. Treatment of *fac*- or *mer*-$[M(CO)_3(\text{dppm-PP}')(\text{dppm-PP})]$ with $Hg(SCN)_2$ in CH_2Cl_2 gives mercury metal and golden yellow crystals of the seven-coordinate Mo(II) complex $[Mo(SCN)_2(CO)_2(\text{dppm-PP}')(\text{dppm-P})]$ in *ca.* 40% yield. This complex has been prepared previously by treating $[MoCl_2(CO)_4]$ with NH_4SCN followed by dppm. The IR data for our compound are very similar to those reported previously [5]. We have determined the crystal structure of our compound which has N-bonded SCN ligands and a geometry similar to several other M(II) complexes (M = Cr, Mo or W) containing CO and PR_3 ligands: see the review by Drew [6].

We find that treatment of $[M^1(CO)_3(\text{dppm-PP}')(\text{dppm-P})]$ with $AgNO_3$ rapidly gives metallic silver and other products, which we have not characterized. Similar treatment with $[(Ph_3P)AgCl]_4$ gives a complex mixture but treatment with $[(Ph_3P)AgCN]$ gives stable, yellow heterobimetacllic complexes of type $[(OC)_3M^1(\mu\text{-dppm})_2AgCN]$ (M^1 = Cr, Mo or W) which have been fully characterized. The $^{31}P\text{-}\{^1H\}$ NMR spectra (at 20 °C) are of the AA'XX' type with further coupling to Ag^{107}, Ag^{109} and W^{183}. The $^1H\text{-}\{^{31}P\}$ NMR spectra at 20 °C show resonances due to both pseudo-equatorial (H_e) or -axial (H_a) PCH_2P hydrogens and only H_e is coupled to silver $^3J(AgPCH_e)$ = 5 Hz for the reasons previously discussed [7]. All three show a single, sharp band due to ν(CN) in the IR spectrum 2042 (Cr), 2044 (Mo) or 2046 (W) cm^{-1}: these frequencies are low for ν(CN) (usually >2100 cm^{-1}) and might indicate a semi-bridging mode, which would explain the presence of non-equivalent methylene protons in the $^1H\text{-}\{^{31}P\}$ NMR spectrum (see above).

Preliminary (NMR) results show that *mer*-$[M^1(CO)_3(\text{dppm-PP}')(\text{dppm-P})]$ (M^1 = Mo or W) react with Ph_3PAuCl to give heterobimetallics containing $[M^1(\mu\text{-dppm})Au]$ moieties with no REDOX behaviour but the complexes have not been characterized.

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