

Reactivity of Phosphido-bridged Heterobinuclear Complexes: Site-selective Carbonyl Substitution by a Hydride. Synthesis and Structural Characterisation of $\text{NEt}_4[\text{H}(\text{CO})_3\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3]$

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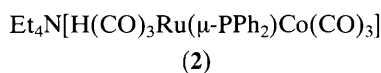
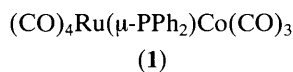
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The phosphido-bridged heterobinuclear compound $(\text{CO})_4\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3$ (**1**) on treatment with NaBH_4 affords, via site-selective CO displacement on the ruthenium atom, the anion $[\text{H}(\text{CO})_3\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3]^-$ which contains a terminal hydride *cis* to a $\mu\text{-PPh}_2$ group: the structure of the anion has been established by an X-ray diffraction study of the Et_4N^+ salt.

Several reactions of considerable interest such as C–C bond formation¹ and ketone synthesis² have been accomplished with transition-metal complexes containing bridging phosphido ligands. Recent reports on unusual transformations of bi- and poly-nuclear $\mu\text{-PR}_2$ complexes³ have focused much attention on the reactivity of these compounds. It has been

established that while a $\mu\text{-PPh}_2$ group may assist in maintaining the structural integrity of a metal framework the phosphido bridge itself may behave as a reactive site in the molecule.^{3,4} In particular, several examples of the conversion of a $\mu\text{-PPh}_2$ group into a terminal PPh_2H ligand by hydridic reducing agents have been described.^{3a,c,d} By contrast, we

observed a significantly different type of behaviour for $(\text{CO})_4\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3$ (**1**) towards sodium borohydride which leads to the formation of the anion $[\text{H}(\text{CO})_3\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3]^-$ *via* a site-selective carbonyl substitution by a hydride. In the complex $\text{Et}_4\text{N}[\text{H}(\text{CO})_3\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3]$ (**2**), which is the first example of a binuclear ruthenium-cobalt compound containing a terminal hydride, the hydride ligand is co-ordinated to the ruthenium *cis* to a $\mu\text{-PPh}_2$ group. In view of the reactivity and the catalytic potential of other hydrido ruthenium carbonyl anions⁵ an abundant chemistry may be expected for (**2**).



Treatment of a suspension of $(\text{CO})_4\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3$ (**1**) (1 mmol), obtained⁶ *via* the reaction of (*p*-cymene)- $\text{RuCl}_2(\text{PPh}_2\text{H})$ with $\text{Co}_2(\text{CO})_8$, in tetrahydrofuran (THF) (70 ml) with an excess of NaBH_4 for 2 h, removal of solvent, and dissolution of the residue in a solution of $[\text{Et}_4\text{N}]\text{Cl}$ (1.5 mmol) in methanol (70 ml) afforded an orange solution from which (**2**) (53%, m.p. 80–82 °C) crystallised. I.r. data [$\nu(\text{CO})$ in THF, 2048m, 1983m, 1963m, 1942w, and 1903m, cm^{-1}] showed only terminal carbonyl absorptions. $^{31}\text{P}\{^1\text{H}\}$ N.m.r. results [$(\text{CD}_2\text{Cl}_2; 213\text{ K}; 32.38\text{ MHz}) \delta 186.5$ (s)] indicated retention of the phosphido bridge across a strong Ru–Co bond⁶ and ^1H n.m.r. data [$(\text{CD}_2\text{Cl}_2; 303\text{ K}) \delta 7.4$ (m, 2 Ph); and -9.25 (d, Ru–H, $^2J_{\text{H-Ru-P}} 22.3\text{ Hz}$)] suggested the presence of a single hydride on the ruthenium atom since no broadening of the hydride resonance due to the ^{59}Co quadrupole was evident. The $^{13}\text{C}\{^1\text{H}\}$ and ^1H coupled n.m.r. spectra were informative: [$^{13}\text{C}\{^1\text{H}\}$ ($\text{CD}_2\text{Cl}_2; 300\text{ K}; 20.45\text{ MHz}) \delta 215.1$ {d, $\text{Co}(\text{CO})_3$, $^2J_{\text{P-C}} 6.8\text{ Hz}$ } 207.3 (d, Ru–CO_{eq-trans}, $^2J_{\text{P-C}} 46.2\text{ Hz}$), 203.1 (s, Ru–CO_{eq-cis}), and 198.3 (d, Ru–CO_{ax-cis}, $^2J_{\text{P-C}} 7.7\text{ Hz}$); $^{13}\text{C}\{^1\text{H}\}$ coupled) $\delta 215.1$ (d), 207.3 (dd, $^2J_{\text{C-H}} 6.8\text{ Hz}$), 203.1 (d, $^2J_{\text{C-H}} 6.0\text{ Hz}$), and 198.3 (dd, $^2J_{\text{C-H}} 27.8\text{ Hz}$); the equatorial plane is defined by the Ru, P, Co atoms, and the *cis*- or *trans*-positions of the carbonyls refer to the PPh_2 group^{6b}]. The stereochemistry of the ruthenium atom with an axial hydride, *cis* to the Ru–Co bond and the $\mu\text{-PPh}_2$ group and *trans* to the axial carbonyl, was indicated by the large $^2J_{\text{H-C}(\text{CO},\text{ax-cis})}$ value and non-equivalence of the phenyl groups. This result was confirmed by a single-crystal X-ray structure determination.† An ORTEP plot of the structure of the anion is shown in Figure 1. The heterobinuclear molecule consists of $\text{Co}(\text{CO})_3$ and $\text{HRu}(\text{CO})_3$ moieties held together by

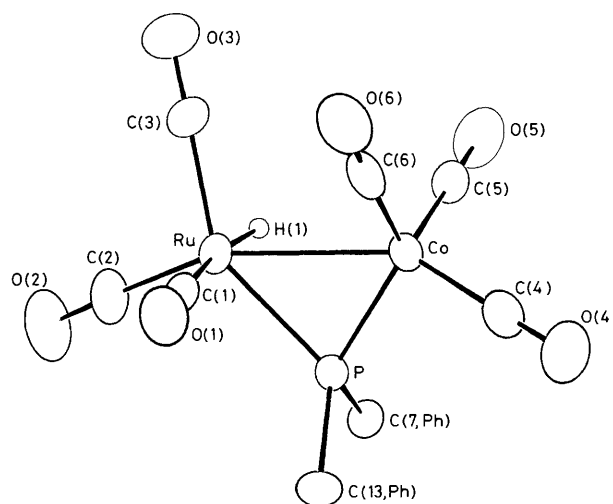


Figure 1. A perspective view of the molecular structure of $\text{Et}_4\text{N}[\text{H}(\text{CO})_3\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3]$ showing the atomic numbering. Important distances not mentioned in the text are: Ru–P 2.307(2), Co–P 2.157(3), Co–C(4) 1.761(10), Co–C(5) 1.795(9), Co–C(6) 1.724(9), Ru–H 1.58 Å.

an Ru–Co bond of length 2.737(1) Å, slightly shorter than that in $(\text{PPh}_3)(\text{CO})_3\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3$ [2.7681(4) Å],⁷ and a phosphido bridge [Ru–P–Co 75.6(1)°]. The stereochemistry at the ruthenium atom is approximately octahedral with the phosphorus atom of the $\mu\text{-PPh}_2$ group, the Ru–Co vector, and two carbonyl groups C(2)–O(2) and C(3)–O(3) defining a distorted plane and with C(1)–O(1) and the hydride H(1) perpendicular to this plane and *trans* to one another [H(1)–Ru–C(1) 167°]. Thus with respect to the Ru–Co and Ru–P bonds, H(1) is axial and *cis*. The terminal hydride exerts a *trans* bond lengthening influence on the carbonyl C(1) with Ru–C(1) [1.957(8) Å] significantly longer than Ru–C(2) [1.848(10) Å] and Ru–C(3) [1.920(9) Å], the latter being *trans* to the $\mu\text{-PPh}_2$ group. There is an interesting comparison with the phosphine derivative $(\text{PPh}_3)(\text{CO})_3\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3$ ⁷ where the PPh_3 ligand occupies an equatorial site *trans* to the Ru–Co bond.

Several observations relating to the substitution of CO in (**1**) by H[−] to give (**2**) can be made. First, the substitution is metal-specific, there being no evidence for a cobalt substitution product. This provides the first evidence for binuclear (Ru–Co) systems⁸ that the known efficacy of ruthenium compounds as hydrogenation catalysts translates into a high affinity for hydride in heterobimetallic species. It is also notable that the small hydride ligand, with a high *trans*-influence, occupies a site other than *trans* to the Ru–Co and Ru–PPh₂ bonds where significant destabilisation of the heterobinuclear molecule by Ru–Co or Ru–P bond lengthening might occur. Finally it is significant that the isolation of (**2**) with *cis*-hydride and $\mu\text{-PPh}_2$ groups on the ruthenium atom, at ambient temperatures provides *both* an indication of a possible mechanism for bridge cleavage *via* PPh_2H elimination and also evidence that hydride attack on heterobinuclear complexes may proceed *without* fragmentation. These observations have obvious relevance to the development of significant chemistry for heterometallic phosphido bridged compounds, a problem which we are currently exploring.

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† *Crystal data*: monoclinic, space group *Cc*, $a = 8.185(1)$, $b = 22.621(3)$, $c = 15.865(2)$ Å, $\beta = 98.67(1)^\circ$, $U = 2903.9(7)$ Å³, $Z = 4$, $D_c = 1.474\text{ g cm}^{-3}$, $F(000) = 1312$ electrons, $\mu(\text{Mo-K}\alpha) = 11.96\text{ cm}^{-1}$. A total of 2572 reflections were measured to $2\theta = 50^\circ$ on a Syntex P2₁ diffractometer. The structure was solved and refined to R and R_w values of 0.035 and 0.043 respectively using 2302 [$I \geq 3\sigma(I)$] observed data. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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