A New Heterobimetallic Zr–Rh Complex, $[\{(\eta^5\text{-}C_5H_5)_2ZrCl(CH_2PPh_2)\}_2\text{-}Rh(CO)Cl]$, leading to an Unexpected Terminal Carbonyl–Zirconium Bond

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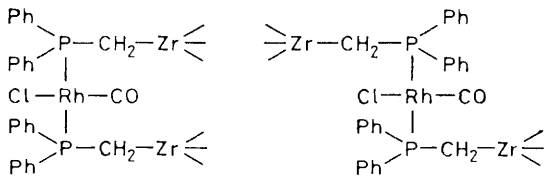
The heterobimetallic complex *trans*-$[\{(\eta^5\text{-}C_5H_5)_2ZrCl(CH_2PPh_2)\}_2Rh(CO)Cl]$ has been prepared and found to react with CO to give unexpectedly the zirconium carbonyl complex $[\{(\eta^5\text{-}C_5H_5)_2Zr(CO)Cl(CH_2PPh_2)\}_2Rh\text{-}(CO)Cl]$; an acyl complex is obtained when the uncomplexed $\{(\eta^5\text{-}C_5H_5)_2ZrCl(CH_2PPh_2)\}$ reacts with CO.

Heterobimetallic complex chemistry is currently being explored with the aim of finding new ways of activating small molecules. The reactivity of species which join an early transition metal (d^0 for instance) to a late one (d^8 for instance) is of great interest but very few examples of them have hitherto been prepared. We report here the synthesis of a new zirconium–rhodium derivative which, because of its unexpected ability to co-ordinate carbon monoxide to zirconium, reacts differently to the uncomplexed starting zirconium derivative.

The phosphinomethyl complex of zirconium(IV), $(\eta^5\text{-}C_5H_5)_2\text{-}ZrCl(CH_2PPh_2)$, (**1**) has recently been prepared and found to react with iron and chromium carbonyls to give spectroscopically characterised bimetallic complexes, $[\{(\eta^5\text{-}C_5H_5)_2\text{-}ZrCl(CH_2PPh_2)\}M(CO)_x]$.[1]

By adding a tetrahydrofuran (THF) solution of $[Rh(CO)_2\text{-}Cl]_2$ to a benzene solution of (**1**) (molar ratio Zr:Rh = 2:1) we obtained, by rapid evaporation, yellow microcrystals of *trans*-$[\{(\eta^5\text{-}C_5H_5)_2ZrCl(CH_2PPh_2)\}_2Rh(CO)Cl]$ (**2**). This new bimetallic complex was characterised by analytical data (Zr, Cl, P, C, H), by i.r. (ν_{CO} 1960 cm^{-1}, C_5H_5 and C_6H_5 bands, and ν_{MCl} 345 cm^{-1}), ^1H n.m.r. [δ 2.16 (dt, 2H, $^2J_{P-H} + {}^4J_{P-H}$ 3.38 Hz, $^3J_{Rh-H}$ 1.17 Hz, CH_2), 5.98 (s, 10H, C_5H_5), and 7.11—7.76 (m, 10H, C_6H_5)], and $^{13}C\{^1H\}$ n.m.r. spectroscopy [δ 14.6 (t, $^1J_{P-C} + {}^3J_{P-C}$ 14.80 Hz, CH_2), 114.5 (s, C_5H_5), 130.3 (s, C_6H_5), 133.6 (t, J_{P-C} 22.2 Hz, C_6H_5), and 133.7 p.p.m. (t, J_{P-C} 6.47 Hz, C_6H_5)], and by comparison with (**1**).†



The room temperature $^{31}P\{^1H\}$ n.m.r. spectrum shows the presence of three rotamers, two of which have equivalent phosphorus nuclei and give A_2X patterns [δ (ext. H_3PO_4) 34.48 ($^1J_{P-Rh}$ 117.19 Hz) or 13.05 p.p.m. ($^1J_{P-Rh}$ 117.19 Hz)] [*e.g.* structure (A)]; the other one has non-equivalent P nuclei and gives an ABX pattern [see structure (B)] [δ 34.35 and 13.85 p.p.m. ($^1J_{P-Rh}$ 120.85 and 120.85, $^2J_{P-P}$ 363.20 Hz)] [see structure (B)]. These data are closely similar to the low temperature

† N.m.r.: ^1H, δ 1.87 (d, $^2J_{H-P}$ 3 Hz, CH_2) and 5.91 (s, C_5H_5); $^{31}P\{^1H\}$, δ 5.95 p.p.m. (s); $^{13}C\{^1H\}$, δ 12.9 (d, $^1J_{C-P}$ 15 Hz, CH_2), and 143.3, 147.0, and 146.3 p.p.m. (3 × s, C_6H_5).

n.m.r. data for the complexes *trans*-$(PXBu^t_2)_2Rh(CO)Cl$.[2] Depending on the synthesis conditions, variable quantities of a fourth rotamer may appear and give an additional ABX pattern [δ 34.76 and 14.41 p.p.m. ($^1J_{P-Rh}$ 119.63 and 122.07, $^2J_{P-P}$ 359.86 Hz)]. The non-equivalence of the phosphorus atoms arises from different arrangements of the phenyl rings, as has been observed in $(PPhBu^t_2)_2Rh(CO)Cl$.[2]

$(\eta^5\text{-}C_5H_5)_2ZrCl(CH_2PPh_2)$

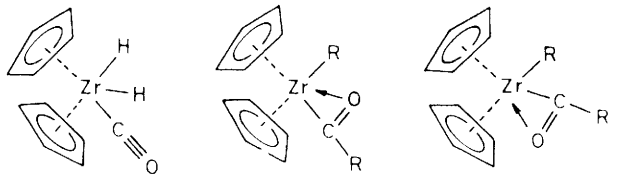
(1)

trans-$[\{(\eta^5\text{-}C_5H_5)_2ZrCl(CH_2PPh_2)\}_2Rh(CO)Cl]$

(2)

In a carbon monoxide atmosphere the uncomplexed zirconium species (**1**) absorbs one mole of CO per mole of (**1**) giving the expected acyl complex $(\eta^5\text{-}C_5H_5)_2ZrCl(COCH_2PPh_2)$ (ν_{CO} 1520 cm^{-1}) as insoluble white crystals, similar to several previously reported η^2-acyl derivatives of zirconium(IV).[3]

In contrast, when the bimetallic complex $[\{(\eta^5\text{-}C_5H_5)_2ZrCl(CH_2PPh_2)\}_2Rh(CO)Cl]$ reacts with CO a new derivative is obtained as a light-brown microcrystalline solid, soluble in common solvents (benzene, THF) but not very stable. The i.r. spectrum shows a new band at ν 2040 cm^{-1} in addition to ν_{Rh-CO} 1960 cm^{-1}. The new band may be attributed to a carbonyl group on the zirconium [*cf.* ν_{Zr-CO} 2044 cm^{-1} in $(\eta^5\text{-}C_5Me_5)_2Zr(CO)H_2$].[4] The formulation of the new derivative as $[\{(\eta^5\text{-}C_5H_5)_2Zr(CO)Cl(CH_2PPh_2)\}_2Rh(CO)Cl]$ is confirmed by n.m.r. data. The ^1H spectrum is not very different from that of (**2**) [C_5H_5 and C_6H_5 unchanged, $\delta(CH_2)$ 2.11]. The ^{31}P spectrum shows only one A_2X pattern: δ 13.25 p.p.m. ($^1J_{P\ Rh}$ 123.56 Hz) very similar to the (A)-type rotamer of (**2**). It may be assumed that (**2**) is more readily attacked by CO, which changes the re-partition between the various conformers present in the solution [a similar change of re-partition increasing the proportion of the (A)-type rotamer also occurs on varying the temperature from +30 to −70 °C]. In the ^{13}C spectrum, the C_5H_5 and C_6H_5 resonances are unchanged compared with (**2**) and CH_2 gives a triplet at δ 14.7 p.p.m. with ($^1J_{P-C} + {}^3J_{P-C}$) 12.0 Hz. When the carbonylation is carried out in a ^{13}CO atmosphere an intense singlet appears at δ 188 p.p.m. which may be attributed to Zr–^{13}CO, while neither the ^{13}C signal for Rh–CO (which would give a doublet with J_{Rh-C} *ca.* 70 Hz)[5], nor the acyl resonance (at *ca.* 300 p.p.m.)[6] is observed.



(C) (D) (E)

As carbonyl derivatives of zirconium(IV) are unknown, except for $(\eta^5\text{-}C_5Me_5)_2Zr(CO)H_2$ which has been spectroscopically characterised[4] at −70 °C, and since acyl derivatives of zirconium(IV) are usually readily obtained, the question of why acyl formation is hindered in the bimetallic complex while the carbonyl is observed (although it is not very stable in solution) remains to be answered.

The reason why (**2**) does not contain stable acyl groups attached to zirconium is probably related to stereochemical factors. It is known that CO co-ordination takes place at an external position, structure (C), and that stable acyl complexes have structure (D); thus rearrangement from (C) to (D) is necessary, probably *via* the unstable structure (E).[6] Such a rearrangement may be impossible in the case of the zirconium–rhodium complex owing to steric hindrance and stereorigidity (demonstrated by slow intramolecular exchange between the rotamers at room temperature).

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