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Preliminary communication

METAL—METAL BONDED RUTHENIUM—MANGANESE COMPLEXES: AN UNEXPECTED PHOSPHIDO-BRIDGED COMPLEX

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Summary

Reactions of $NaMn(CO)_5$ with $RuCl_2(PMe_3)_4$, $RuCl_2(dppm)_2$ and $RuCl_2(PPh_3)_3$ lead either to an ionic species $[Ru_2Cl_3(PMe_3)_6]^+ [Mn(CO)_5]^-$ or to metal—metal bonded Ru—Mn compounds such as $RuMn(\mu\text{-}CO)_2(CO)_3(\mu\text{-}dppm)_2Cl$, and, quite unexpectedly, to the μ-phosphido complex $RuMn(\mu\text{-}PPh_2)(CO)_6(PPh_3)_2$ via a hydride intermediate.

The preparation and reactivity of heterobimetallic complexes are much studied because of the potential use of such compounds for bimetallic activation and catalysis. In the activation of carbon monoxide, the association of two metals of different oxophilicity can result in CO coordination at two centres, a promising method of enhancing reactivity and promoting new types of reactions [1].

We chose to prepare ruthenium—manganese complexes as the more oxophilic of the two metals (manganese) does not give too strong a metal oxygen bond, thus allowing the possibility of catalytic reactions. We describe here the reactions of $NaMn(CO)_5$ with $RuCl_2(PPh_3)_3$, $RuCl_2(PMe_3)_4$ and $RuCl_2(dppm)_2$ (dppm = $Ph_2PCH_2PPh_2$) and the products thus obtained.

Metathetical reaction of $NaMn(CO)_5$ * with $RuCl_2(PPh_3)_3$ produces two compounds: one is easily identified by IR and ^{31}P NMR spectral data as the known $Ru(CO)_3(PPh_3)_2$ [2] the other, obtained as red crystals from toluene/hexane in moderate yield (ca. 30%) analyses (C, H, P, Mn) for $RuMn(\mu\text{-}PPh_2)(CO)_6(PPh_3)_2$ (1). The presence of both Ru and Mn in a single crystal has been established by EDAX** 1 shows five ν(CO) bands in its IR

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*All reactions were performed at room temperature in THF by addition of one equivalent of ruthenium dichloride complex to a freshly prepared solution of $NaMn(CO)_5$.

**EDAX = Energy dispersive analysis by X-rays.

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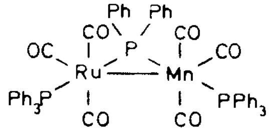


(1)

spectrum at 2050(s), 1960(s), 1947(m), 1920(vs) and 1843(vs) cm^{-1} (vaseline mulls) and an ABC pattern in its ^{31}P {^{1}H} NMR spectrum at −80°C, as can be seen in Fig. 1; at room temperature, there is a broadening of the peaks P_{Mn} and P_μ due to the quadrupolar ^{55}Mn nucleus. This and the analogy of chemical shift and coupling constant with the PPh$_3$ on ruthenium in RuCo(μ-PPh$_2$)(CO)$_5$(PPh$_3$)$_2$ [3] indicate that 1 has a phosphido group (P_μ) *trans* to two phosphorus one (P_{Ru}) on ruthenium and the other (P_{Mn}) on manganese, in contrast with the *cis*-PPh$_3$ on Co for RuCo(μ-PPh$_2$)(CO)$_5$(PPh$_3$)$_2$.

The chemical shift of the phosphido group is close to the values between PPh$_2$ groups bridging a metal—metal bond (δ 50, 300) and those not bridging (δ 50, −200), [3] but still favours a metal—metal bond, which would be in agreement with the diamagnetism of the proposed formulation.

Although several examples of phosphido-bridged heterobimetallic complexes have been recently reported [3,4], the formation of 1 was totally unexpected: starting from a dichloro compound, a chloride bridged manganese—ruthenium complex seemed more likely. Elimination of C$_6$H$_6$ from hydridotriphenylphosphine complexes are known to give phosphido groups [3,5]; in our case C$_6$H$_6$ was detected by GLC in the filtrate, and the formation of the PPh$_2$ group may be explained by the intermediate formation of a

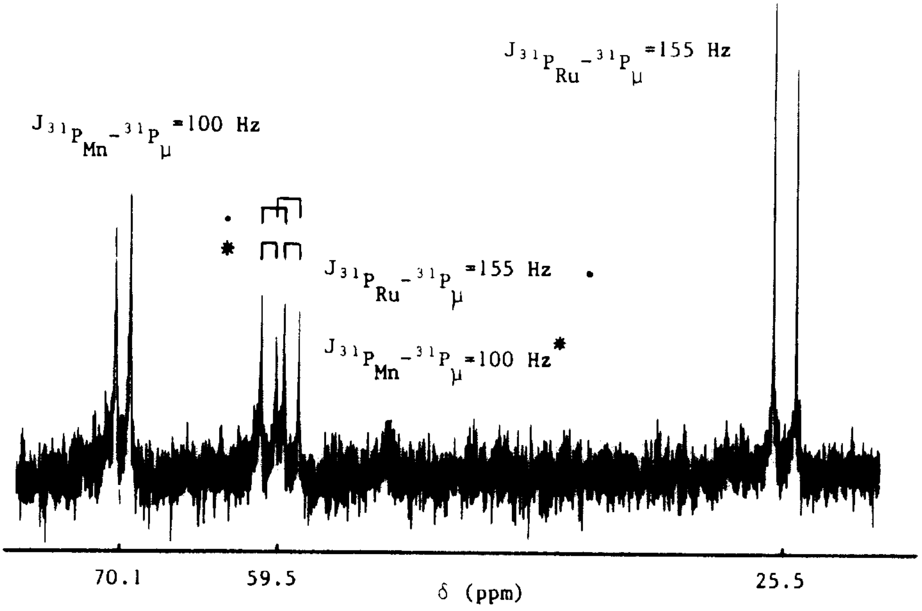
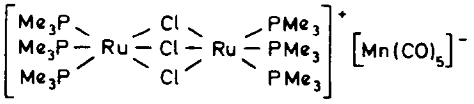


Fig. 1. ^{31}P {H} NMR spectrum of RuMn(μ-PPh$_2$)(CO)$_6$(PPh$_3$)$_2$ in toluene-d_8 solution at −80°C (positive δ values to high frequency relative to external H$_3$PO$_4$) recorded at 101.270 MHz.

hydrido complex. In fact, the ^1H and ^{31}P NMR spectra of the reaction mixture show the presence of $RuHCl(CO)_2(PPh_3)_2$, as revealed by comparison with reported data [3], together with two other unidentified hydride species in small amount (^1H NMR δ −6.6 (triplet) and −13.4 (multiplet) ppm).

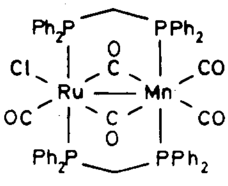
Thus, unexpectedly, the reaction products obtained by action of $NaMn(CO)_5$ on $RuCl_2(PPh_3)_3$ namely $Ru(CO)_2(PPh_3)_3$, $RuHCl(CO)_2(PPh_3)_2$ and the μ-phosphido complex are quite similar to those obtained by Geoffroy from the reaction of $NaCo(CO)_4$ with $RuHCl(CO)(PPh_3)_3$ [3]. Such complexes, containing a phosphido bridge together with a metal—metal bond, are particularly suitable for catalytic transformation since the bridging ligand is able to hold the metals together while the metal—metal bond can be cleaved and reformed by successive oxidative addition and eliminative reduction in the catalytic sequence.



(2)

Upon performing the same reaction with $RuCl_2(PMe_3)_4$ we obtained as the major product yellow crystals of a very air sensitive compound analysing (C, H, P, Mn) for $[Ru_2Cl_3(PMe_3)_6][Mn(CO)_5]$ (2). Conductivity measurements in acetone demonstrate that the complex is a 1/1 conductor; the ^{31}P NMR spectrum exhibits a singlet at δ 18.9 ppm and the IR spectrum shows two bands at 1890(vs) and 1850(vs) cm^{-1}, close to those reported for $Mn(CO)_5^-$. Thus the product is not a bimetallic complex but an ionic species: after abstraction of one chlorine atom to give NaCl, the very stable triply chloro-bridged diruthenium cation has been formed and $Mn(CO)_5^-$ left as counteranion. This type of dinuclear cation is very common in ruthenium chemistry, although as far as we know it has never been prepared before with PMe_3 ligands [6].

With the aim of preparing bimetallic complexes in which a diphosphine may act as a bridging ligand with the same catalytic potentiality as a phosphido bridge, we also treated *cis*-$RuCl_2(dppm)_2$ with $NaMn(CO)_5$. After two days, two products were isolated: a very air sensitive yellow product (3) and a moderately air sensitive red product (4). With increase in the reaction time (ca. 10 days), 4 became the major product and was recrystallized from THF/hexane. The yellow species 3 is probably again an ionic complex, and is tentatively formulated as $[RuCl(dppm)_2(THF)]^+[Mn(CO)_5]^-$ from IR (two $\nu(CO)$ bands at 1905(vs) and 1855(vs) cm^{-1}) and ^{31}P NMR (single peak at δ −14 ppm) spectroscopy.



(4)

The red product 4 analysing (C, H, P, Cl, Mn) for RuMn(μ-CO)$_2$(CO)$_3$-(μ-dppm)$_2$Cl is more interesting. EDAX spectroscopy on a single crystal confirms the presence of both Ru and Mn. The ^{31}P NMR spectrum shows, as in related bimetallic complexes [7], an AA'MM' pattern at δ (P_{Ru}) 36.0 and δ (P_{Mn}) 57.9 ppm (broadening due to the quadrupolar ^{55}Mn nucleus is still observed). Its IR spectrum shows five ν(CO) bands at 1940(s), 1895(vs), 1870(s), 1720(m), 1710(m) cm^{-1} in vaseline mull and at 1925(m), 1895(vs), 1870(s), 1720(m,broad) in CH_2Cl_2 solution. We propose for this compound a structure involving two bridging dppm groups, two bridging CO groups, and a metal—metal bond.

The low bridging CO stretching frequency is the same as that found recently in a dinuclear manganese compound [8]. This type of structure (bimetallic complex bridged by two *trans* dppm groups) is now well known for the platinum metal homonuclear complexes, and examples of similar heterobimetallic complexes have also been recently reported [7,9].

These preliminary results show that it is possible to prepare metal—metal bonded ruthenium—manganese complexes, but they need to be stabilized by bridges of the type PR_2 or dppm. This stabilization will allow the study of the reactions of these new species in which the bimetallic frame is preserved.

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References

1 D.A. Roberts and G.L. Geoffroy in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, 1982, Chapter 40.

2 B.E. Cavit, K.R. Grundy and W.R. Roper, J. Chem. Soc. Chem. Commun., (1972) 60.

3 H.C. Foley, W.C. Finch, C.G. Pierpont and G.L. Geoffroy, Organometallics, 1 (1982) 1379.

4 M.J. Breen, G.L. Geoffroy, A.L. Rheingold and W.C. Fultz, J. Am. Chem. Soc., 105 (1983) 1069 and ref. therein.

5 B.N. Chaudret, D.J. Cole-Hamilton, R.S. Nohr and G. Wilkinson, J. Chem. Soc. Dalton Trans., (1977) 1546.

6 J. Chatt and R.G. Hayter, J. Chem. Soc., (1961) 896; M.S. Lupin and B.L. Shaw, J. Chem. Soc. A, (1970) 63; P.W. Armit, A.S.F. Boyd and T. Stephenson, J. Chem. Soc. Dalton Trans., (1975) 1663.

7 P.G. Pringle and B.L. Shaw, J. Chem. Soc. Dalton Trans., (1983) 889; D.M. Mc Ewan, P.G. Pringle and B.L. Shaw, J. Chem. Soc. Chem. Commun., (1982) 859; W.S. McDonald, P.G. Pringle and B.L. Shaw, ibid., (1982) 861.

8 F.M. Ashmawy, C.A. Mc Auliffe, K.L. Minten, R.V. Parish and J. Tames, J. Chem. Soc. Chem. Commun., (1983) 436.

9 P. Braunstein, J.M. Jud and J. Fischer, J. Chem. Soc. Chem. Commun., (1983) 5; B. Chaudret, B. Delavaux and R. Poilblanc, Nouv. J. Chim., in press.