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METATHETICAL REACTIONS OF CARBONYLATE ANIONS WITH DICHLORORUTHENIUM COMPLEXES: PREPARATION AND CHARACTERIZATION OF RUTHENIUM–MOLYBDENUM AND RUTHENIUM–MANGANESE COMPLEXES

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Summary

The possibility of making metal–metal bonded heterobimetallic species by metathesis of ruthenium dichlorides with anionic carbonylates is demonstrated by the isolation of $MoRu(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2(PPh_3)_2(\eta\text{-}C_5H_5)$ (**1**) and $MnRuCl(\mu\text{-}CO)_2(CO)_3(\mu\text{-}dppm)_2$ (**2**), obtained by action of $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ on $RuCl_2(PPh_3)_3$ and of $Mn(CO)_5{}^-$ on $RuCl_2(dppm)_2$, respectively. In contrast, reaction of $Mn(CO)_5{}^-$ with $RuCl_2(PMe_3)_4$ yielded an ionic species **3** containing the diruthenium cation $Ru_2Cl_3(PMe_3)_6{}^+$. More interestingly, the action of $Mn(CO)_5{}^-$ on $RuCl_2(PPh_3)_3$ resulted in the formation of the unexpected complex $MnRu(\mu\text{-}PPh_2)(CO)_6(PPh_3)_2$ (**4**) in which the phosphido group PPh_2 bridges the two metals; this process is shown to involve a hydride intermediate, and elimination of a molecule of benzene, both identified in the reaction mixture.

The preparation and reactivity of heterobimetallic complexes are presently widely studied largely because of their possible catalytic activity [1] but very few such complexes containing ruthenium are known *. As part of an exploration of routes to ruthenium-containing heterobimetallic complexes we have examined some metathesis reactions between $NaMn(CO)_5$ or $NaMo(CO)_3(\eta\text{-}C_5H_5)$ and various chlororuthenium complexes. We chose manganese and molybdenum as the second metal as

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* As far as metathetical reactions are concerned, one ruthenium-containing heterobimetallic complex [2] has been obtained, by reaction of $RuHCl(CO)(PPh_3)_3$ with $NaCo(CO)_4$, and clusters [3] have been made by reaction of $NaCo(CO)_4$ with chlororuthenium(III) complexes.

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they are oxophilic but not too markedly so, so that complexes of this type should be ideal candidates for CO reduction. We found that heterobimetallic complexes were obtained in three cases, although not easily and not always with the expected formula. A preliminary account of the results has appeared [4].

Results and discussion

Metathesis Reaction of NaMo(CO)$_3$(η-C$_5$H$_5$) with RuCl$_2$(PPh$_3$)$_3$. Reaction of the anion $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ with $RuCl_2(PPh_3)_3$ in tetrahydrofuran (THF) leads to elimination of NaCl and one triphenylphosphine ligand to give a violet solid unambiguously analysing for $MoRuCl(CO)_3(PPh_3)_2(\eta\text{-}C_5H_5)$ (**1**).

The complex was characterized by spectroscopic methods (Tables 1 and 2). The ^{1}H NMR spectrum confirms the presence of both η-C$_5$H$_5$ and PPh$_3$ ligands (integration ratio: Cp/PPh$_3$ 1/2). The single resonance at δ 49.3 ppm in the

TABLE 1

MICROANALYTICAL DATA [a] FOR COMPLEXES 1–4

Complex	M	P	C	H	Cl
1	10.57	6.57	58.46	3.96	3.35
	(10.60) [b]	(6.85)	(58.31)	(3.87)	(3.92)
2	4.74	10.09	59.10	4.24	3.51
	(5.00) [c]	(11.28)	(60.03)	(3.64)	(3.23)
3	6.05	20.30			
	(5.73) [c]	(19.39)			
4	4.92	8.18	65.00	4.12	<1
	(4.89) [c]	(8.27)	(65.07)	(4.27)	(0)

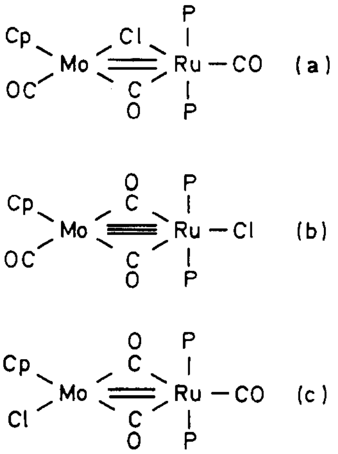
[a] Analysis (%); calculated values in parentheses. [b] M = Mo. [c] M = Mn.

TABLE 2

PHYSICAL DATA FOR COMPLEXES 1–4

Complex	ν(CO) (cm^{-1})	^{1}H NMR δ(ppm), J(Hz) [c]	^{31}P NMR δ(ppm), J(Hz)
1	1930, 1830, 1775 [a,b]	$\delta_{(\eta\text{-}C_5H_5)}$ 5.0	49.3 [d]
2	1940(s), 1895(vs), 1870(s), $\underbrace{\text{1720(m), 1710(m)}^{a}}_{1720^{b}}$	$\left\{\begin{array}{l}\delta(H_a)\ 3.8\\ \delta(H_e)\ 2.9\\ J(H-H)\ 13\end{array}\right.$	$\left\{\begin{array}{l}\delta(P_{Ru})\ 36.0^{e}\\ \delta(P_{Mn})\ 57.9\end{array}\right.$
3	1890(s), 1860(s) [a]		18.9 [e]
4	2050(s), 1960(s), 1947(m), 1920(vs), 1843(vs) [a] 2055(s), 2045(s), 1945(vs), 1920(vs), 1845(vs) [a] 2050(s), 1970(s), 1925(vs), 1850(s) [b]	$\left\{\begin{array}{l}\delta(P(1))\ 25.5^{f}\\ \delta(P(2))\ 59.5\\ \delta(P(3))\ 70.1\\ J(P(1)-P(2))\ 155\\ J(P(2)-P(3))\ 100\end{array}\right.$	

[a] In Nujol. [b] In CH$_2$Cl$_2$. [c] In C$_6$D$_6$. [d] In C$_7$D$_8$. [e] In THF/C$_6$D$_6$. [f] In THF/C$_7$D$_8$.



SCHEME 1. Proposed structures for $MoRuCl(CO)_3(PPh_3)_2(\eta\text{-}C_5H_5)$ (spectroscopic data lead us to favour structure (a): see text) ($Cp = (\eta\text{-}C_5H_5)$, $P = PPh_3$).

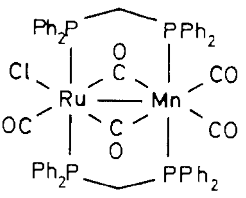
$^{31}P\{^1H\}$ NMR spectrum from 293 to 188 K is consistent with two equivalent PPh_3 ligands bonded to ruthenium, probably in a *trans* configuration. The $^{13}C\{^1H\}$ spectrum shows a singlet for the Cp carbons at δ 92.3 ppm and a single broad peak for the carbonyl ligands at δ 232 ppm; this implies fluxionality of the molecule. The IR spectrum does not show any band attributable to a terminal M–Cl stretch but three bands in the carbonyl region at 1930, 1830, and 1775 cm^{-1}.

In the light of these data, three structures are possible (Scheme 1). Structure (**c**), which contains a 16-electron molybdenum moiety and a terminal Mo–Cl bond, is not very likely. Structure (**b**), which includes a terminal Ru–Cl bond and a 16-electron ruthenium moiety, also seems unlikely; for as noted above, no M–Cl stretch is observed in the infrared and the values of the carbonyl frequencies are in agreement with a terminal CO on ruthenium (1930 cm^{-1}), a terminal CO on molybdenum (1830 cm^{-1}), and a bridging CO (1775 cm^{-1}). Furthermore, **1** does not react with H_2 at room temperature, whereas a 16-electron ruthenium moiety would be expected to do so.

For all these reasons we prefer structure (**a**); this, like the Rh–Mo complex recently reported by Carlton et al. [5], could contain a double metal–metal bond and thus have an 18-electron configuration around each metal atom.

The presence of two different ligands bridging the metal–metal bond, viz. chloride and carbonyl, seem unusual but in the absence of X-ray crystal structure determination, this seems to us the most reasonable proposal.

Metathesis reaction of $NaMn(CO)_5$ with $RuCl_2(dppm)_2$ (dppm = $Ph_2PCH_2PPh_2$). The anion $[Mn(CO)_5]^-$ reacts with *cis*-$RuCl_2(dppm)_2$ in THF to give, after a prolonged reaction (ca. 10 days), a low yield of red crystals analysing for $MnRuCl(CO)_5(dppm)_2$ (**2**) (Tables 1 and 2). The $^{31}P\{^1H\}$ NMR spectrum is characteristic of two bridging dppm ligands, since it is an AA′MM′ spin system [6]. There is broadening of the resonances of the ^{31}P nuclei attached to the quadrupole ^{55}Mn nucleus. The ^1H NMR spectrum shows two PCH_2P resonances at room temperature and the $^1H\{^{31}P\}$ NMR spectrum is resolved into an AB pattern with $^2J(H\text{–}H)$ 13 Hz as a result of the inequivalence of the pseudo-equatorial hydrogen

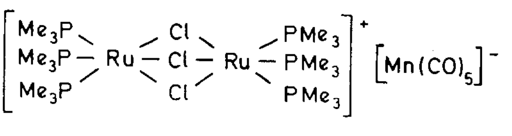


(2)

H_e and the pseudo-axial hydrogen H_a: this is a feature which Shaw et al. have previously noted, but at lower temperatures [7]. The IR spectrum exhibits ν(CO) bands of terminal (1940, 1895, and 1870 cm^{-1}) as well as bridging (1720 and 1710 cm^{-1}) carbonyl ligands. A band at 360 cm^{-1} can be attributed to a terminal chlorine ligand attached to Ru. Taking account of all the data we propose a structure for **2** which involves two bridging dppm groups, two bridging carbonyl groups, and a metal–metal bond, in keeping with the diamagnetism of the complex. This provides an 18-electron environment for both Mn and Ru.

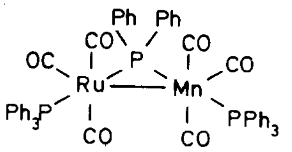
If the reaction time is reduced (ca. 2 days), a mixture of complex **2** with another product is obtained. The latter is a very air-sensitive yellow product tentatively formulated as $[RuCl(dppm)_2(THF)]^+[Mn(CO)_5]^-$ from IR (two ν(CO) bands at 1905 and 1855 cm^{-1} characteristic of the anion $[Mn(CO)_5]^-$ and ^{31}P NMR (one single peak at δ -14 ppm). This complex may be an intermediate for the formation of **2**. The slow step is then probably decoordination of one phosphine group of dppm and the substitution of one carbonyl group of manganese.

Formation of an ionic species from $NaMn(CO)_5$ *and* $RuCl_2(PMe_3)_4$. Reaction of $[Mn(CO)_5]^-$ with $RuCl_2(PMe_3)_4$ does not give the expected bimetallic complex but instead the ionic species $[Ru_2Cl_3(PMe_3)_6]^+[Mn(CO)_5]^-$ (**3**), as very air-sensitive yellow crystals. This complex has been characterized by elemental analysis, conductivity measurements in acetone (Λ 70 Ω^{-1} cm^2 mol^{-1}, 1/1 conductor), IR spectrum (ν(CO) at 1890 and 1860 cm^{-1} for the anion $[Mn(CO)_5]^-$) and a single resonance in the $^{31}P\{^1H\}$ NMR spectrum (all the PMe_3 ligands are equivalent) (Tables 1 and 2). After abstraction of one chlorine atom to give NaCl, a stable triply chloro-bridged diruthenium cation has been formed and $[Mn(CO)_5]^-$ left as counter anion. The X-ray crystal structure of the cation $[Ru_2(\mu\text{-}Cl)_3(PMe_3)_6]^+$, with $[BF_4]^-$ as counter-anion, has been recently reported [8].



(3)

Unexpected formation of a phosphido-bridged complex by reaction of $RuCl_2(PPh_3)_3$ *with* $NaMn(CO)_5$. In contrast with the preceding case, addition of $RuCl_2(PPh_3)_3$ to $[Mn(CO)_5]^-$ in THF leads, after NaCl elimination, to red crystals analysing for $MnRu(PPh_2)(CO)_6(PPh_3)_2 \cdot C_6H_5CH_3$ (**4**). The formulation of complex **4** follows



(4)

from elemental analysis, EDAX *, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ NMR, and IR spectroscopy (Tables 1 and 2). The $^{31}P\{^1H\}$ NMR spectrum at −80°C exhibits an ABC pattern with a doublet at $\delta(P(1))$ 25.5 pppm, a doublet of doublet at $\delta(P(2))$ 59.5 ppm, and a doublet at $\delta(P(3))$ 70.1 ppm, with $J(P(1)-P(2))$ 155 Hz and $J(P(2)-P(3))$ 100 Hz. At room temperature there is a broadening of the peaks P(2) and P(3) due to the quadrupolar ^{55}Mn nucleus, while the peak P(1) remains unchanged. Thus P(1) can be attributed to a PPh_3 ligand on Ru, P(3) to a PPh_3 ligand on Mn, and P(2) to a phosphido group PPh_2^- bridging the two metals. The high values of the coupling constants indicate that the two phosphine ligands are *trans* to the phosphido group, whereas for $RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$ one phosphine is *trans* and the other *cis* to the phosphido [2]. The chemical shift of the phosphido group is consistent with the presence of a metal–metal bond, which provides an 18-electron environment for both Mn and Ru [2,9].

The IR spectra of **4** show $\nu(CO)$ bands typical of terminal carbonyl ligands ($> 1800\ cm^{-1}$). In the solid state, two isomers can be distinguished, whereas in CH_2Cl_2 solution only one of them is seen. It is possible that *cis* and *trans* isomerism are present in the solid state, but in solution only the *trans* isomer is present, as confirmed by ^{31}P NMR.

The $^{13}C\{^1H\}$ NMR spectrum of **4** exhibits two broad signals at 201 and 196 ppm: each of these can be attributed to three terminal carbonyl ligands attached to each metal, the molecule being non-rigid.

Other products, **5** and **6**, can be identified in the reaction mixture:

$$RuCl_2(PPh_3)_3 + NaMn(CO)_5 \rightarrow$$

$$\underset{\textbf{(4)}}{MnRu(\mu\text{-}PPh_2)(CO)_6(PPh_3)_2} + \underset{\textbf{(5)}}{RuHCl(CO)_2(PPh_3)_2} +$$

$$\underset{\textbf{(6)}}{Ru(CO)_3(PPh_3)_2} + \ldots + C_6H_6 + \ldots + NaCl$$

Thus the products are quite similar to those obtained by Geoffroy et al. [2] from the reaction of $NaCo(CO)_4$ with $RuHCl(CO)(PPh_3)_3$ yielding $RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$ together with **5**, **6**, C_6H_6, NaCl. In our case the unexpected formation of a phosphido group from a dichloro ruthenium complex, $RuCl_2(PPh_3)_3$ can be explained in terms of the intermediate formation of a hydride complex [10], according to Scheme 2.

We detected complex **5** in the reaction mixture as well as other unidentified hydride species, by ^1H NMR (δ −6.6 ppm (t), −13.4 ppm (m)); C_6H_6 was detected by GLC in the filtrate.

Reaction of $RuHCl(PPh_3)_3$ with $NaMn(CO)_5$. The study of this system was

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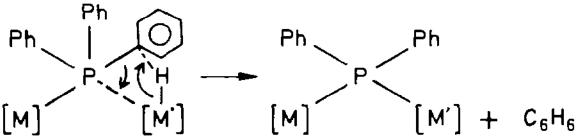
* EDAX = energy dispersive analysis by X-rays.



SCHEME 2

undertaken with the hope of obtaining the complex **4** in better yield when starting from a hydride complex of ruthenium. In fact, the product mixture was even more complicated than before. Complex **4** was obtained in low yield and various by-products were identified, e.g. $Ru(CO)_3(PPh_3)_2$, $RuHCl(CO)_2(PPh_3)_2$, $RuH_2(CO)_2(PPh_3)_2$, and $MnH(CO)_3(PPh_3)_2$. Finally, a new yellow bimetallic species was detected by EDAX and by IR spectroscopy (ν(CO) at 1975, 1970, 1950, 1890 cm^{-1}), but it co-crystallized with $Ru(CO)_3(PPh_3)_2$ and could not be isolated pure.

Hydroformylation catalytic tests. The catalytic activity of $MnRu(\mu\text{-}PPh_2)(CO)_6(PPh_3)_2$ and $MnRuCl(CO)_5(\mu\text{-dppm})_2$ as hydroformylation catalyst was examined using pentene-1 at constant pressure of 40 bar and temperature of 80°C with 1/1 H_2/CO gas mixture (0.07 mmol **4** or **2**, 18 mmol pentene-1, 15 cm^3 C_6H_6). After 18 h, only 2% conversion (selective n-hexanal) was obtained.

$Mn_2(CO)_{10}$ [11] and $Ru(CO)_4(PPh_3)$ [12] were identified from the IR spectrum of the reaction mixture obtained after catalysis with **4**; the bimetallic structure has been broken down.

Conclusion

We have succeeded in preparing one ionic and three true heterobimetallic complexes. In only one case (with $NaMo(CO)_3(\eta\text{-}C_5H_5)$) did the reaction follow the expected route. The preparation of a phosphido-bridged complex is interesting but not unusual; it cannot be regarded as a general synthetic procedure. The most interesting and promising reaction is perhaps the coupling of metathesis with the use of bridging ligands, even though the reaction was very slow in the case of the preparation of $MnRuCl(CO)_5(dppm)_2$.

The low reactivity of these complexes (no reaction with H_2; very poor activity as hydroformylation catalysts) is probably related to their electronic saturation. We plan now to concentrate on the preparation of coordinatively unsaturated species containing bridging ligands.

Experimental

All manipulations were carried out under argon in conventional Schlenk apparatus, using solvents dried by distillation before use and deoxygenated. Microanalyses were performed by the Centre d'Analyse du CNRS or in this laboratory. Infrared spectra were obtained as Nujol mulls using a Perkin–Elmer 225 instrument. NMR spectra were recorded on a Bruker WH90 or WM250 spectrometer operating in the Fourier-transform mode.

The complexes $RuCl_2(PPh_3)_3$, $RuCl_2(dppm)_2$, and $RuHCl(PPh_3)_3$ were prepared by published methods [13–15]. $RuCl_2(PMe_3)_4$ was prepared by reaction of four equivalents of PMe_3 with $RuCl_2(dmso)_4$ [16]. The sodium salts $NaMo(CO)_3(\eta\text{-}C_5H_5)$ and $NaMn(CO)_5$ in THF solutions were freshly prepared by published methods [17,18].

$[MoRu(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2(PPh_3)_2(\eta\text{-}C_5H_5)]$ (1). A solution of $NaMo(CO)_3(\eta\text{-}C_5H_5)$ (from $(Mo(CO)_3(\eta\text{-}C_5H_5))_2$, 0.94 mmol) in THF (30 cm^3) was added to $RuCl_2(PPh_3)_3$ (1.46 g, 1.52 mmol) in THF (20 cm^3). The color immediately turned violet. The mixture was stirred overnight at room temperature, then the solvent was removed under vacuum and the soluble products extracted with toluene. After filtration and evaporation to ca. 30 cm^3, **1** slowly precipitated out as a violet solid (yield ca. 40%).

$[MnRuCl(\mu\text{-}CO)_2(CO)_3(\mu\text{-}dppm)_2]$ (2). A solution of $NaMn(CO)_5$ (from $Mn_2(CO)_{10}$, 1.4 mmol) in THF (30 cm^3) was added to $RuCl_2(dppm)_2$ (0.98 g, 1 mmol) in THF (100 cm^3). The mixture was stirred for 10 days, during which the colour changed from yellow to red. The volume was reduced, the mixture was filtered, and hexane was added. The solution was cooled to $-30°C$ to give red crystals of **2** after a long time (ca. 10 days) (yield ca. 10–20%).

$[Ru_2(\mu\text{-}Cl)_3(PMe_3)_6]^+[Mn(CO)_5]^-$ (3). A solution of $NaMn(CO)_5$ (from $Mn_2(CO)_{10}$, 0.93 mmol) in THF (30 cm^3) was added to $RuCl_2(PMe_3)_4$ (0.44 g, 0.93 mmol) in THF (20 cm^3). The mixture was stirred overnight, then filtered. The volume was reduced and the solution was cooled to $-30°C$ to give ochre crystals of **3**.

$[MnRu(\mu\text{-}PPh_2)(CO)_6(PPh_3)_2 \cdot C_6H_5CH_3]$ (4). $RuCl_2(PPh_3)_3$ (1.47 g, 1.53 mmol) was added to a solution of $NaMn(CO)_5$ (from $Mn_2(CO)_{10}$, 0.77 mmol) in THF (30 cm^3) at room temperature. The mixture was stirred for 20 h and then evaporated to dryness. The soluble products were extracted with toluene and the solution was filtered. Addition of hexane and cooling to $-30°C$ gave red crystals of **4** (yield ca. 30%). The presence of a toluene molecule of crystallization was revealed by microanalysis and the ^1H NMR spectrum. Changing the addition order of the starting materials or using two equivalents of $NaMn(CO)_5$ did not give a better yield. Complex **4** did not react with H_2 at room temperature and ordinary pressure.

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