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LETTER

Heterobimetallic Complexes via *fac*-$Mo(CO)_3(\eta^2\text{-bpy})(\eta^1\text{-dppm})$: Complexes of Tin, Mercury or Rhodium Derivatives

M. CANO*, J. A. CAMPO, P. OVEJERO and J. V. HERAS
Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid (Spain)

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Bis(diphenylphosphine)methane (dppm) has a strong tendency to act as a monodentate or as a bridging bidentate ligand. The free phosphorus atom in η^1-dppm complexes may be used as a ligand to the same or to a different metal atom. But, it is the ability of dppm to form bridged binuclear complexes that has led to the recent interest in these and related ligands.

Reactions of group VI metal carbonyl bis(diphenylphosphine)methane of the type *fac*-$[M(CO)_3(\eta^2\text{-dppm})(\eta^1\text{-dppm})]$ with labile carbonyl compounds of Rh(I) or Ir(I) have been described, to give heterobimetallic complexes containing $[M(\mu\text{-dppm})_2M']$ (M' = Rh, Ir) groups. Similar dppm chelate ring-opening reactions are induced with Ag(I), Cu(I) or Au(I) derivatives, giving heterobimetallic species. However, when Hg(II) salts are used, different behaviour is observed and mononuclear Mo(II) complexes such as $[Mo(CO)_2(X)_2(\eta^2\text{-dppm})(\eta^1\text{-dppm})]$ (X = Cl, SCN) are obtained [1].

We report here the reactivity of related $[Mo(CO)_3(\eta^2\text{-bpy})(\eta^1\text{-dppm})]$ (bpy = 2,2'-bipyridine) complexes towards Rh(I), Hg(II), Sn(II) and Sn(IV) derivatives in order to find the possibility of the formation of new heterobimetallic species through a dppm bridging ligand.

We found contrasting behaviour when Sn or Hg halides were used with respect to the reaction with $[RhCl(NBD)]_2$ (NBD = norbornadiene). In the first case, the oxidation of $Mo(CO)_3(\eta^2\text{-bpy})(\eta^1\text{-dppm})$ to binuclear Mo(II) complexes was observed, depending on the solvent employed. In the second case, a compound containing the $[Rh(\mu\text{-dppm})Mo]$ moiety was proposed.

Treatment of *fac*-$[Mo(CO)_3(\eta^2\text{-bpy})(\eta^1\text{-dppm})]$ with $SnCl_4$ in dichloromethane yielded the known compound $[Mo(CO)_3(\eta^2\text{-bpy})(SnCl_3)(Cl)]$ [2]; however, when acetone was used a new complex $[Mo(CO)_2(\eta^2\text{-bpy})(\eta^2\text{-dppm})\cdot 2SnCl_4]$ was obtained. The new compound shows two carbonyl stretching bands at 1952 and 1888 cm^{-1} in the IR spectrum (in KBr pellets). The ^{31}P NMR spectrum in $CDCl_3$ shows only a signal at $\delta = 38.6$ ppm, consistent with the presence of two equivalent phosphorus atoms of a bidentate dppm ligand. The molar conductivity measurements in acetone solution ($\Lambda_m = 128.5$ ohm^{-1} cm^2 mol^{-1}) are indicative of a 1:1 electrolyte, and the diamagnetic behaviour agrees with the presence of Mo(II). Thus, an ionic formulation of the type $[Mo(CO)_2(\eta^2\text{-bpy})(\eta^2\text{-dppm})(SnCl_3)][SnCl_5]$ could be suggested for this compound.

Treatment with $HgCl_2$ in dichloromethane at room temperature also gives an oxidation product. This fact could be deduced by the increase observed in the absorption frequencies of the carbonyl groups [$\nu(C\equiv O) = 1950, 1935, 1830$ cm^{-1}] with respect to the initial compound [$\nu(C\equiv O) = 1908, 1805, 1780$ cm^{-1}]. These data are very similar to those reported before for $[Mo(CO)_3(\eta^2\text{-NN})]_2(HgCl_2)$ [3–5]. The low solubility of the isolated compound makes its study difficult. However, the ^{31}P NMR spectrum in DMSO-d_6 shows a broad hump which is indicative of the presence of coordinated phosphorus and should be attributed to the formation of coordination products of the type $HgCl_2(dppm)$. Additional studies are necessary in order to elucidate this behaviour.

On the other hand, the reaction of *fac*-$Mo(CO)_3(\eta^2\text{-bpy})(\eta^1\text{-dppm})$ with $[RhCl(NBD)]_2$ in dichloromethane gives $[(OC)_3(\eta^2\text{-bpy})Mo(\mu\text{-dppm})Rh(CO)Cl]$. The new complex presents low solubility at room temperature. The proposed formulation and the assignment of a structure like that proposed in Fig. 1 was made on the basis of spectroscopic data. Its intense blue–violet colour and the formation of a metallic mirror in the flask suggest a metal–metal bond, which is in agreement with the formation of a 34 e^- species. The IR spectrum in KBr pellets shows absorptions at 1985(sh), 1970(vs), 1900(vs), 1780(sh) and 1755(vs) cm^{-1}. The lowest frequency band is

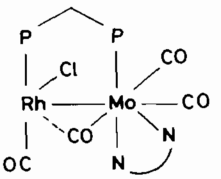

Fig. 1. Probable structure of $[(OC)_3(\eta^2\text{-bpy})Mo(\mu\text{-dppm})Rh(CO)Cl]$.

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*Author to whom correspondence should be addressed.

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characteristic of a semibridging CO group [6], and the other absorptions are assigned to terminal CO groups bonded at rhodium and molybdenum. The ^{31}P NMR spectrum shows two broad resonances in the region of coordinated phosphorus. An exact interpretation could not be realized because the signals are broad and there is poor resolution of the resonances; NMR spectral data at low temperature are necessary. We are trying to obtain additional information on these compounds.

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