# Syntheses and Dynamic Stereochemistry of Methyl– and Phenyl–Carbonyl Heterobinuclear Metal–Metal Bonded Complexes

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The bimetallic complexes $[\mathrm{ML}_n\mathrm{PtMe(PPh_3)_2}]$ $[\mathrm{ML}_n = \mathrm{Mo(CO)_3(\eta\text{-}C_5H_5)}, \mathrm{W(CO)_3(\eta\text{-}C_5H_5)}, \mathrm{Mn(CO)_5}$, or $\mathrm{Co(CO)_4}]$ and $[\mathrm{ML}_n\mathrm{PtPh(PPh_3)_2}]$ $[\mathrm{ML}_n = \mathrm{Mo(CO)_3(\eta\text{-}C_5H_5)}$ or $\mathrm{W(CO)_3(\eta\text{-}C_5H_5)}]$ have been prepared by the reaction of the *in situ* generated $[\mathrm{Pt(OClO_3)R(PPh_3)_2}]$ (R = Me or Ph) with the appropriate carbonylmetalate anions. The complexes $[(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_3\mathrm{MoPtMe(PPh_3)_2}]$ and $[(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_3\mathrm{WPtMe(PPh_3)_2}]$ show low-temperature $^{31}$P n.m.r. spectra consistent with a *cis* structure. A reversible, mutual exchange process is observed upon warming, but already at room temperature, solutions of $[(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_3\mathrm{MoPtMe(PPh_3)_2}]$ show a *cis–trans* isomerization process. In contrast, the other bimetallic complexes are rigid in solution, displaying a *trans* configuration.

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Heterobimetallic complexes containing both early and late transition metals have been the subject of much current interest.[1] Many of these complexes undergo interesting fluxional processes in solution[2–7] whose study is relevant to the reactivity and site selectivity exhibited by heterometallic complexes.[8] This is the case, for example, for the recently reported compounds $[\mathrm{MPt(H)(\eta\text{-}C_5H_5)(CO)_3(PPh_3)_2}]$ (M = Mo or W) and $[\mathrm{MnPt(\mu\text{-}H)(\mu\text{-}CO)(CO)_4(PEt_3)_2}]$.[7]

As an extension of the latter studies, we became interested in determining the influence of the replacement of the hydrido ligand by R groups on the synthesis and dynamic properties of such complexes. We report here the preparation and dynamic

**Table.** Spectroscopic data

| Complex | $T$/K | I.r. $\nu$(CO)/cm$^{-1}$ | $^{31}$P-{$^1$H} N.m.r.* $\delta(\mathrm{P_a})$ | $\delta(\mathrm{P_b})$ | $\delta$(P) | $J(\mathrm{P_a}$–Pt) | $J(\mathrm{P_b}$–Pt) | $J$(P–Pt) |
|---|---|---|---|---|---|---|---|---|
| *cis*-(**1**) | 195 | 1 910vs<br>1 820s<br>1 780s | 36.7 | 32.7 | | 3 215 | 3 124 | |
| *trans*-(**1**) | 309 | 1 930s<br>1 830s,br | | | 35.2 | | | 2 963 |
| *cis*-(**2**) | 195 | 1 910vs<br>1 810s<br>1 770s | 36.7 | 32.1 | | 3 230 | 3 143 | |
| *trans*-(**3**) | 240 | 2 026m<br>1 992vs<br>1 960s<br>1 919vs,br<br>1 884s | | | 28.4 | | | 3 077 |
| *trans*-(**4**) | 240 | 2 015s<br>1 949vs<br>1 943 (sh)<br>1 804s<br>1 797s | | | 30.8 | | | 2 975 |
| *trans*-(**5**) | 195 | 1 910s<br>1 840s<br>1 800s | | | 22.0 | | | 3 150 |
| *trans*-(**6**) | 195 | 1 910s<br>1 830s<br>1 795s | | | 22.5 | | | 2 758 |

* δ Values in p.p.m., $J$ in Hz.

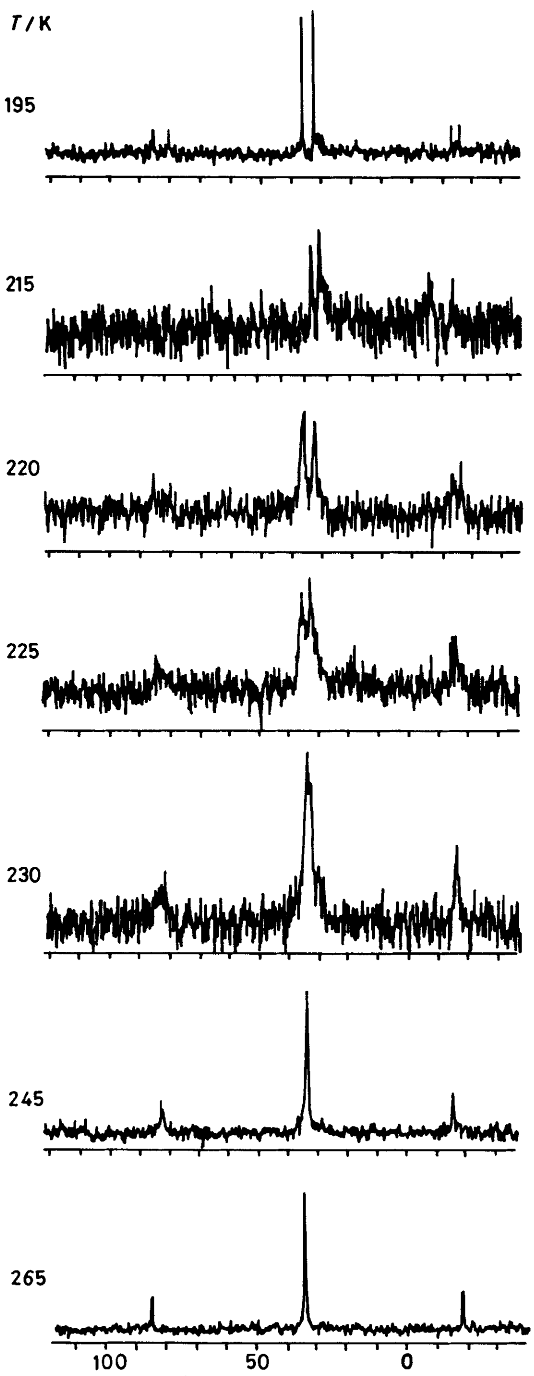

**Figure.** Variable-temperature $^{31}P$-$\{^1H\}$ n.m.r. spectra of $[(\eta\text{-}C_5H_5)(CO)_3MoPtMe(PPh_3)_2]$

properties of several bimetallic complexes of the type $[ML_nPtR(PPh_3)_2]$ [R = Me or Ph; $ML_n = Mo(CO)_3(\eta\text{-}C_5H_5)$, $W(CO)_3(\eta\text{-}C_5H_5)$, $Mn(CO)_5$, or $Co(CO)_4$].

## Results and Discussion

The reaction of a toluene solution of $[Pt(OClO_3)R(PPh_3)_2]$ (R = Me or Ph) with one equivalent of the sodium salt of each of the carbonylmetalate anions $[M(CO)_3(\eta\text{-}C_5H_5)]^-$ (M = Mo or W), $[Mn(CO)_5]^-$, or $[Co(CO)_4]^-$ in tetrahydrofuran (thf) at −78 °C afforded, after stirring for 1 h, the new heterobimetallic complexes $[ML_nPtR(PPh_3)_2]$ according to equation (1).

$$[Pt(OClO_3)R(PPh_3)_2] + Na[ML_n] \xrightarrow{-78\,^{\circ}C} [ML_nPtR(PPh_3)_2] + Na(ClO_4) \quad (1)$$

**(1)** R = Me; $ML_n = Mo(CO)_3(\eta\text{-}C_5H_5)$
**(2)** R = Me; $ML_n = W(CO)_3(\eta\text{-}C_5H_5)$
**(3)** R = Me; $ML_n = Mn(CO)_5$
**(4)** R = Me; $ML_n = Co(CO)_4$
**(5)** R = Ph; $ML_n = Mo(CO)_3(\eta\text{-}C_5H_5)$
**(6)** R = Ph; $ML_n = W(CO)_3(\eta\text{-}C_5H_5)$

Attempts to obtain analogous bimetallic compounds containing the bulkier pentachlorophenyl group failed. After stirring for 3 h at room temperature, no reaction took place between $[Pt(OClO_3)(C_6Cl_5)(PPh_3)_2]$ and $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$ in thf or toluene solution.

All complexes are unstable to air as solids and in solution, and satisfactory elemental analyses were obtained only for (**1**) and (**4**). Spectroscopic parameters are presented in the Table.

The $^{31}P$ n.m.r. spectra of (**1**) and (**2**) at 195 K show two sets of resonances [$^2J(P\text{–}P) \approx 0$], each flanked with platinum satellites, indicating a *cis* arrangement of inequivalent $PPh_3$ ligands bonded to platinum.

Both complexes present variable-temperature $^{31}P$ n.m.r. spectra indicative of a dynamic behaviour. A complete set of variable-temperature $^{31}P$ n.m.r. spectra for (**1**), directly obtained from the reaction solution, is shown in the Figure. The low-temperature spectra are fully consistent with a static solution structure similar to that found in the crystalline state of *cis*-$[(\eta\text{-}C_5H_5)(CO)_3MoPtH(PPh_3)_2]$.[7] Upon warming, these lines begin to collapse and a broad resonance midway between both lines appears. Above 230 K it sharpens into a singlet. During this process, the satellite resonances are maintained and follow a comparable change. These spectral changes are reversible on recooling the sample. The dynamic behaviour of (**1**) and (**2**) is concentration independent, ruling out a bimolecular exchange process. The retention of spin coupling in the high-temperature $^{31}P$ n.m.r. spectra clearly indicates that this equivalencing of the two phosphine ligands on the n.m.r. time-scale is an intramolecular process. Reasonable explanations for the phosphine exchange mechanism on the n.m.r. time-scale may be put forward on the basis of related studies on *cis*-$[ML_nPtH(PR'_3)_2]$ [$ML_n = Mo(CO)_3(\eta\text{-}C_5H_5)$ or $Mn(CO)_5$; R′ = Ph or Et][7] and *cis*-$[PtH(SiR'_3)(PPh_3)_2]$[9] (R′ = Ph, $C_6H_4Cl$-*p*, or $C_6H_4Me$-*p*) complexes.

In contrast to the results for (**1**) and (**2**), complexes (**3**)—(**6**) are rigid in solution. In these cases, the singlet line measured directly for the reaction solutions at 195 K is indicative of a *trans* arrangement of the phosphines and remains unaltered in the temperature range 195—270 K. Therefore it can be deduced that in this series of complexes, the stereochemistry of the final products is kinetically controlled by the nature of the ligands attached to platinum. This idea is strengthened by the observation that when a solution of (**1**) is allowed to reach room temperature a new signal appears, after several hours, in the $^{31}P$ n.m.r. spectrum (Table). We assign this resonance, and its platinum satellites, to *trans*-(**1**) and formation of this isomer does not reverse upon lowering the temperature. It has not been possible to isolate the *trans* isomer of (**1**) in a pure form owing to its high tendency to decompose. On the other hand, there is no evidence for the formation of *trans*-(**2**) after allowing the toluene solutions of the *cis* isomer to reach room temperature. Decomposition has precluded its characterization and corresponds to a lower stability of the bimetallic tungsten derivatives with respect to their molybdenum analogues.

In these studies, we have found that steric factors play a considerable role in determining the stereochemistry and the stability of the bimetallic complexes.

## Experimental

Solvents were dried by standard methods, and all manipulations and reactions were performed in Schlenk-type flasks under nitrogen. Elemental C and H analyses were carried out at the Institut de Bio-Orgànica de Barcelona.The $^1H$ and $^{31}P-\{^1H\}$ n.m.r. spectra were measured on a Bruker WP 80SY spectrometer. Positive phosphorus chemical shifts are downfield relative to external $H_3PO_4$. Infrared spectra were recorded on a Perkin-Elmer 1330 spectrophotometer with KBr pellets.

Compounds $[PtI(Me)(PPh_3)_2]$[10] and $[PtCl(Ph)(PPh_3)_2]$[11] were prepared as described previously. The sodium salts of $[Co(CO)_4]^-$ and $[Mn(CO)_5]^-$ were prepared by Na–Hg reduction of the corresponding binuclear complexes. The salts $Na[M(CO)_3(\eta\text{-}C_5H_5)]\cdot 2dme$ (M = Mo or W, dme = 1,2-dimethoxyethane) were obtained by direct synthesis.[12]

*Preparation of Solutions of* $[Pt(OClO_3)R(PPh_3)_2]$ (R = Me *or* Ph).—$AgClO_4$ (1.0 mmol) was added to a solution of $[PtI(Me)(PPh_3)_2]$ or $[PtCl(Ph)(PPh_3)_2]$ (1.0 mmol) in toluene (30 $cm^3$) at room temperature. After a few minutes, the AgX formed was filtered off. The resulting solutions were kept in the freezer.

*Preparation of the Complexes* $[ML_nPtR(PPh_3)_2]$ [R = Me, $ML_n$ = $Mo(CO)_3(\eta\text{-}C_5H_5)$, $W(CO)_3(\eta\text{-}C_5H_5)$, $Mn(CO)_5$, *or* $Co(CO)_4$; R = Ph, $ML_n$ = $Mo(CO)_3(\eta\text{-}C_5H_5)$, *or* $W(CO)_3(\eta\text{-}C_5H_5)$].—All these compounds were prepared by the following general method. The appropriate carbonylmetalate anion (0.6 mmol) in thf solution (25 $cm^3$) was added dropwise to a solution of $[Pt(OClO_3)R(PPh_3)_2]$ (0.6 mmol) in toluene (30 $cm^3$) at $-78$ °C. The resulting mixture was allowed to react for 1 h and then an equal volume of precooled hexane was added. The yellow powder precipitated was collected by filtration and washed with deoxygenated water (3 × 20 $cm^3$) to eliminate the alkali salts and dried *in vacuo* [Found: C, 54.9; H, 3.9. Calc. for $C_{47}H_{38}MoO_3P_2Pt$ (**1**): C, 55.2; H, 3.9. Found: C, 53.8; H, 3.6. Calc. for $C_{41}H_{33}CoO_4P_2Pt$ (**4**): C, 54.3; H, 3.6%].

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