Facile dynamical intramolecular exchange of a phosphine ligand between two different metal atoms†

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The cluster complex $PtRu_5(CO)_{15}(PMe_2Ph)(\mu_6\text{-}C)$ has been shown to exhibit facile intramolecular exchange of the phosphine ligand between a platinum and ruthenium atom that is rapid on the NMR timescale at 160 °C.

The ability of polynuclear metal complexes to rearrange their ligand frameworks is central to understanding their reactivity.[1] Today, there are many examples of dynamical exchange of ligands between metal atoms in polynuclear metal complexes.[1,2] CO, CNR and NO ligands are the most common examples of ligands that undergo these exchange processes intramolecularly. Although there is evidence that phosphine ligands may change sites between metal atoms in polynuclear metal complexes,[3] there has heretofore been only one demonstrated example of the *intramolecular* exchange of phosphine ligand between two metal atoms that is rapid on the NMR timescale.[4] Here, we report the first example of facile intramolecular exchange of a phosphine ligand between two different metal atoms in a heteronuclear metal cluster complex.

Reaction of the complex $PtRu_5(CO)_{16}(\mu_6\text{-}C)$ **1**[5] with PMe_2Ph at 25 °C has yielded two new complexes, $PtRu_5(CO)_{15}(PMe_2Ph)(\mu_6\text{-}C)$ **2** (36% yield) and $PtRu_5(CO)_{14}(PMe_2Ph)_2(\mu_6\text{-}C)$ **3** (45% yield).‡ Compounds **2** and **3** were characterized by a combination of IR,§ NMR§ and single-crystal X-ray diffraction analyses.¶ The molecular structures of **2** and **3** are shown in Figs. 1 and 2, respectively. Both compounds are structurally similar to that of **1** and consist of an octahedral cluster containing one platinum and five ruthenium atoms and a single
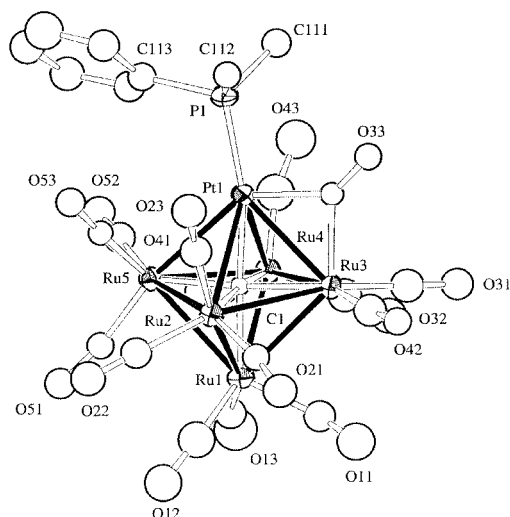

Fig. 1 An ORTEP diagram of the molecular structure of $PtRu_5(CO)_{15}(PMe_2Ph)(\mu_6\text{-}C)$, **2** showing 40% probability thermal ellipsoids. Selected bond distances (Å) and angles (°): Pt(1)–P(1) 2.26(1), Pt(2)–P(2) 2.27(1); Ru(3)–Pt(1)–P(1) 144.5(3), Ru(5)–Pt(1)–P(1) 123.5(3), Ru(10)–Pt(2)–P(2) 145.4(4), Ru(8)–Pt(2)–P(2) 123.6(3).
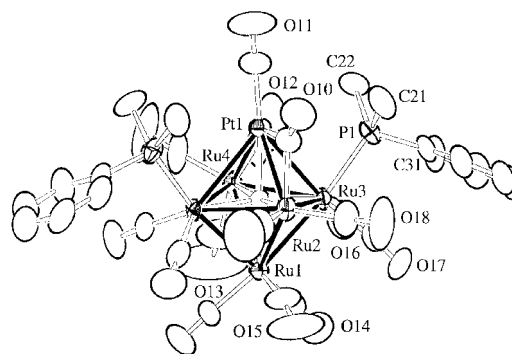
Fig. 2 An ORTEP diagram of the molecular structure of $PtRu_5(CO)_{14}(PMe_2Ph)_2(\mu_6\text{-}C)$ **3** showing 40% probability thermal ellipsoids. Selected bond distances (Å) and angles (°): Ru(3)–P(1) 2.344(2); Pt(1)–Ru(3)–P(1) 81.60(6).

carbon atom in the center. The PMe_2Ph ligand is terminally coordinated to the platinum atom in **2**, while in compound **3** the two PMe_2Ph ligands are both coordinated to ruthenium atoms on opposite sides of the cluster. In both compounds there is a bridging carbonyl ligand between the platinum atom and one of the ruthenium atoms.

The ^{31}P NMR spectrum of **2** indicates that it exists in solution as a mixture of two isomers in a 7:3 ratio at 25 °C. The resonance of the major isomer, $\delta -10.52$, shows large coupling ($^1J_{PtP}$ 6084 Hz) to the platinum atom indicating that the P and Pt atoms are mutually bonded. By contrast, a small coupling ($^2J_{PtP}$ 115 Hz) to the ^{195}Pt in the phosphorus resonance of the minor isomer, δ 9.51, indicates that the phosphorus atom is co-ordinated to one of the neighboring ruthenium atoms. This is supported by the ^{31}P NMR spectrum of compound **3** which shows that **3** exists as a mixture of three isomers in solution. One isomer (40% abundance) shows only a single phosphorus resonance with a small ^{195}Pt–^{31}P coupling of 139 Hz. This is assigned to the isomer as found in the solid state that has equivalent phosphine ligands on separate ruthenium atoms. The major isomer (50% abundance) and the minor isomer (10% abundance) both show two phosphorus resonances. For both isomers there is one resonance with large ^{195}Pt –^{31}P coupling, $^1J_{PtP}$ 5999 Hz (major) and $^1J_{PtP}$ 6111 Hz (minor), and one resonance with small coupling, ^{195}Pt–^{31}P, $^2J_{PtP}$ 63 Hz for the major isomer (in the minor isomer the ^{195}Pt–^{31}P coupling was too small to measure). It is proposed that one PMe_2Ph ligand is coordinated to the platinum atom and one PMe_2Ph ligand is coordinated to a ruthenium atom in these two isomers.

^1H NMR spectra of the methyl resonances of **2** at various temperatures are shown in Fig. 3.‖ At 25 °C, two resonances are observed: δ 1.78 (d, 6H, CH_3, $^2J_{PH}$ 10, $^3J_{PH}$ = 53 Hz) (major isomer) and δ 1.98 (d, 6H, CH_3, $^2J_{PH}$ 10 Hz) (minor isomer). The major isomer shows significant ^{195}Pt–^1H coupling. No ^{195}Pt–^1H coupling was observed for the minor isomer. This is consistent with our interpretation of the ^{31}P NMR spectra of **2**. It was observed that the resonances of both isomers broaden and coalesce, reversibly, as the temperature is raised, and most importantly, ^{195}Pt satellites are observed on the resonances in
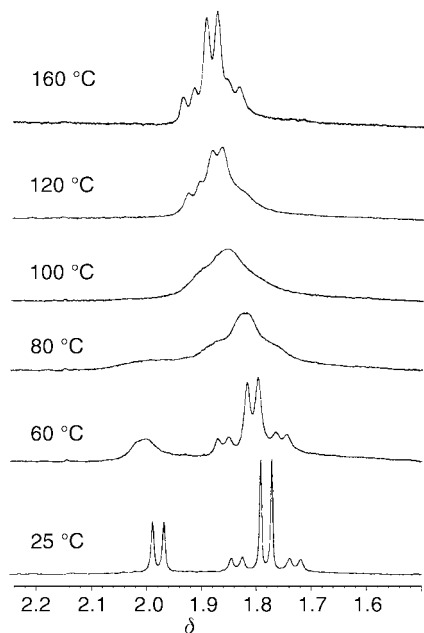
Fig. 3 ^{1}H NMR spectra of compound **2** at various temperatures in 1,2-C$_6$D$_4$Cl$_2$ solvent.

the averaged spectrum at 160 °C. The ^{195}Pt–^{1}H coupling of 41 Hz observed at 160 °C is a weighted average of the ^{195}Pt–^{1}H coupling of the two isomers.** These spectra confirm the existence of a dynamical isomerization process by which the phosphine ligand interchanges coordination sites between the platinum atom and one of the ruthenium atoms in **2**, and the observation of the ^{195}Pt–H coupling in the averaged spectra confirms that the process is intramolecular.[6] The exchange broadened spectra were simulated by line shape calculations∥ that have provided exchange rates and in turn activation parameters for the process, $\Delta H^{\ddagger} = 15.1(3)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -7.7(9)$ cal K^{-1} mol^{-1} for the transformation of the major isomer to the minor isomer, and $\Delta H^{\ddagger} = 14.5(3)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -11.4(9)$ cal K^{-1} mol^{-1} for the transformation of the minor isomer to the major isomer.**

A mechanism to explain these observations is shown in Fig. 4. The structure of the major isomer is represented in diagram **2a**. The proposed structure of the minor isomer is represented in diagram **2b**. The dynamical isomerization between **2a** and **2b** can be explained by a shift of the phosphine ligand from the platinum atom to one of the neighboring ruthenium atoms. It is proposed that the phosphine ligand is shifted to the ruthenium atom positioned opposite to that containing the bridging carbonyl ligand. The process may be initiated by a series of CO ligand shifts that traverse the intermediate **A**. To form **A** from **2a**, the bridging CO ligand is shifted to a terminal position on the platinum atom and two terminal CO ligands on ruthenium atoms are shifted to bridging positions across two adjacent Ru–Ru bonds. The structure of **A** is analogous to that of the compound PtRu$_5$(CO)$_{14}$(PPh$_2$CH$_2$CH$_2$PPh$_2$)(μ_6-C) **4** recently reported by Lee and Shapley in which both phosphorus atoms of the chelating ligand are coordinated to the platinum atom.[7] The
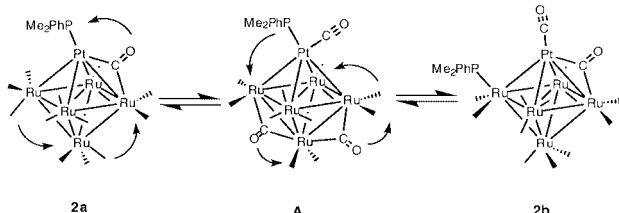

Fig. 4 A proposed mechanism for the isomerization of two isomers of compound **2** by intramolecular shifts of the phosphine and carbonyl ligands between the metal atoms. The carbon atom in the center of the cluster is omitted for clarity.

exchange process is completed by a shift of the phosphine ligand from the platinum atom to the ruthenium atom. The bridging CO ligands are shifted to terminal positions as indicated by the arrows in **A** and a terminal CO ligand is moved into a bridging position across the same Pt–Ru bond that contained the bridging CO ligand in **2a**.

Notes and references

‡ A 12.6 mg amount of **1** (0.011 mmol) was allowed to react with 1.2 μL of PMe$_2$Ph (0.014 mmol) in 15 mL of CH$_2$Cl$_2$ at 25 °C for 30 min. Separation by TLC in air using hexane solvent yielded 3.9 mg of **2** (36% yield) and 5.2 mg of **3** (45% yield).
§ *Spectral data*: for **2**: IR ν_{CO}/cm^{-1} (CH$_2$Cl$_2$): 2085m, 2066 (sh), 2054vs, 2037vs, 1995 (sh), 1852w, br. ^{1}H NMR (in 1,2-dichlorobenzene-d$_4$): major isomer **2a**: minor isomer **2b** = 7:3 at 25 °C. For **2a**: δ 1.78 (d, 6H, CH$_3$, $^2J_{PH}$ 10, $^3J_{PtH}$ 53 Hz); ^{31}P{^{1}H} NMR (in 1,2-dichlorobenzene-d$_4$): δ −10.52 ($^1J_{PtP}$ 6084 Hz). For **2b**: ^{1}H NMR (in 1,2-dichlorobenzene-d$_4$): δ 1.98 (d, 6H, CH$_3$, $^2J_{PH}$ 10 Hz); ^{31}P{^{1}H} NMR (in 1,2-dichlorobenzene-d$_4$): δ 9.51 ($^2J_{PtP}$ 115 Hz). For **3**: IR ν_{CO}/cm^{-1} (in CH$_2$Cl$_2$): 2069m, 2021vs, 1968 (sh), 1811w, br. ^{1}H NMR (in 1,2-dichlorobenzene-d$_4$): 50% isomer: δ 1.85 (d, 6H, CH$_3$, $^2J_{PH}$ 9.8, $^3J_{PtH}$ 51.0 Hz), 1.51 (d, 6H, CH$_3$, $^2J_{PH}$ 10.8 Hz). 40% isomer: δ 1.94 (d, 6H, CH$_3$, $^2J_{PH}$ 9.5 Hz). 10% isomer: δ 1.75–2.04, J_{PtH} and J_{PH} were obscured in this region. ^{31}P{^{1}H} NMR (in 1,2-dichlorobenzene-d$_4$): 50% isomer: δ −13.45 (d, $^1J_{PPt}$ 5999, J_{PP} 8 Hz), 9.62 (d, J_{PtP} 63, J_{PP} 8 Hz). 40% isomer: δ 4.35 (s, $^2J_{PPt}$ 139 Hz). 10% isomer: δ −11.80 (d, $^1J_{PtP}$ 6111, J_{PP} 7 Hz), −1.11 (d, J_{PP} 7 Hz).
¶ *Crystal data*: for **2**: PtRu$_5$PO$_{15}$C$_{24}$H$_{11}$, M_r = 1270.76, orthorhombic, space group *Pna*2$_1$, a = 44.897(5), b = 14.590(2), c = 10.208(2) Å, V = 6687(2) Å^3, T = 20 °C, μ = 6.47 mm^{-1}, R_1 = 0.050, R_2 = 0.080. Two structurally similar independent molecules in the asymmetric crystal unit; anisotropic refinement on Pt, Ru and P only.

For **3**: PtRu$_5$P$_2$O$_{14}$C$_{37}$H$_{28}$, M_r = 1459.01, monoclinic, space group *P*2$_1$/*m*, a = 9.407(1), b = 25.955(7), c = 9.980(1) Å, β = 113.41(1)°, V = 2236.0(7) Å^3, T = 20 °C, μ = 4.88 mm^{-1}, R_1 = 0.034, R_2 = 0.046. Compound **2** has mirror symmetry in the solid state; anisotropic refinement of all non-hydrogen atoms.

CCDC 182/1610. See http://www.rsc.org/suppdata/cc/b0/b001080o/ for crystallographic files in .cif format.
∥ Lineshape simulations of spectra in the exchange broadened region were preformed by using the program EXCHANGE written by R. E. D. McClung, Dept. of Chemistry, University of Alberta, Edmonton, Alberta, Canada. Variable temperature ^{1}H NMR spectra of compound **3** show that it is also undergoing dynamical processes indicative of rapid phosphine ligand exchanges.
** A plot of the temperature dependence of the equilibrium, minor isomer to major isomer, provided the thermodynamic parameters ΔH° = 0.58(8) kcal mol^{-1} and ΔS° = 3.7(3) cal K^{-1} mol^{-1}. From these parameters the ratio of the major isomer/minor isomer is calculated to be 3.3:1 at 160 °C. From this ratio, the weighted average of the ^{195}Pt–^{31}P coupling constant is calculated to be 40.7 Hz.

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