Trapping a pseudo-Hofmann rearrangement on a ruthenium cluster†

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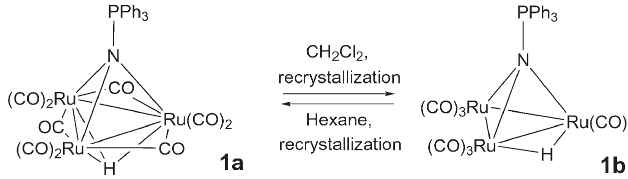
In the clusters $[Ru_3(\mu_3\text{-}NPPh_3)(\mu_3\text{-}OSiMe_3)(\mu\text{-}X)(\mu_{C,O}\text{-}OC{=}NPPh_3)(\mu\text{-}CO)(CO)_6]$ (X = NCO, 2; X = Cl, 3), which were prepared by a pyrolytic reaction of $Ph_3PNSiMe_3$ with $Ru_3(CO)_{12}$, the ligands result from a cluster-mediated pseudo-Hofmann rearrangement involving the μ-NCO, μ(C,O)-$Ph_3P{=}N\text{–}CO$ and μ_3-$NPPh_3$ fragments.

The isomeric clusters $[Ru_3(\mu_3\text{-}H)(\mu_3\text{-}NPPh_3)(\mu\text{-}CO)_3(CO)_6]$ (**1a**) and $[Ru_3(\mu\text{-}H)(\mu_3\text{-}NPPh_3)(CO)_9]$ (**1b**), obtained by the reaction of $[Ru_3(CO)_{12}]$ with $Ph_3P{=}NSiMe_3$, are unusual in that their reversible interconversion is exclusively solvent-dependent, as shown in Scheme 1.[1]

Although related precedents have been reported,[2] this remains a very rare phenomenon. Surprisingly, **1a** could not be detected spectroscopically in any solvent, including that from which it was crystallized, raising an interesting question about the relationship between solid-state structure and reactivity in solution.

The reaction of $Ph_3P{=}NSiMe_3$ with finely dispersed $[Ru_3(CO)_{12}]$ in CH_2Cl_2 at 130 °C in a sealed tube originally afforded **1a** and **1b**, but if two more equivalents of $Ph_3P{=}NSiMe_3$ were added to the mixture and heating was continued for another 2 h, two new clusters, $[Ru_3(\mu_3\text{-}NPPh_3)(\mu_3\text{-}OSiMe_3)(\mu\text{-}X)(\mu_{C,O}\text{-}OC{=}NPPh_3)(\mu\text{-}CO)(CO)_6]$ (X = NCO, **2**; X = Cl, **3**), were formed. Although they were isolated in low yields, their structural characterization has revealed unprecedented ligand rearrangements and structural characteristics. Preparative thin-layer chromatography allowed the separation of clusters **2** and **3** as the only products that could be isolated.†‡ Although pure **2** could not be separated from **3**, single crystals were obtained from a solution containing both clusters. X-Ray diffraction studies revealed the co-crystallization of **2** and **3** in a 2 : 3 ratio.§ Subsequently, cluster **3** was obtained pure by increasing the reaction time, and its structure was solved independently.¶ The molecular structures of clusters **2** and **3** are depicted in Fig. 1 and Fig. 2, respectively.



Scheme 1

The two structures are closely related. A Ru_3 open triangle is symmetrically capped by a Ph_3PN group and a Me_3SiO ligand. In cluster **2**, the Ru···Ru edges are bridged by a Ph_3PNCO, a CO and a NCO group. In cluster **3**, the isocyanate is replaced by a chlorine atom. The coordination of the metal centres is completed by six terminal COs. Clusters **2** and **3** should be regarded as containing only one formal metal–metal bond, the Ru(2)–Ru(3) bond, since its length in **3** is 2.8627(7) Å, in contrast to the Ru(1)···Ru(2) and Ru(1)···Ru(3) distances of 3.2337(6) and 3.1175(7) Å, respectively. Following the EAN rules, this implies a total electron count (TEC) of 52, which can be accounted-for by considering the Me_3SiO ligand as a 5 electron donor and the other bridging ligands, Ph_3PN, Cl and Ph_3PNCO, as 3 electron donors (in their neutral forms). The electronic situation for the μ_3-$NPPh_3$ ligand deserves comment. Whereas the radical $Ph_3P{=}\ddot{N}^{\bullet}$ can behave as a 3 electron donor, a $P^+\text{–}N^-$ formalism emphasizes its possible behaviour as a 5 electron donor. A related approach can be applied to the isoelectronic μ_3-methylphenylsulfoximido ligand, PhMeS(=O)N.[3] The consistency between the crystal structures and the TEC of 52 qualitatively suggests that the former approach is more appropriate in the present case. However, the orbital analysis of cluster model **5** (see below) suggests that the P–N bond order is

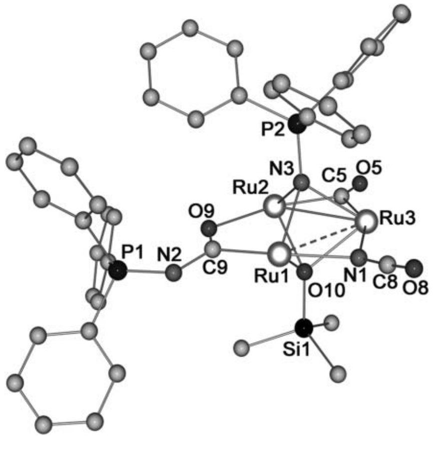


Fig. 1 View of the molecular structure of compound **2** co-crystallized with compound **3**. The terminal carbonyls (two for each Ru atom) and hydrogens have been omitted for clarity. Except for those involving the N(1)C(8)O(8) ligand, bond distances and angles are analogous to those of **3** and are reported in the ESI.†

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† Electronic supplementary information (ESI) available: Spectroscopic, crystallographic and DFT details, Cartesian atomic coordinates of the DFT models and outputs, and ORTEP views with thermal ellipsoids. See DOI: 10.1039/b611338a

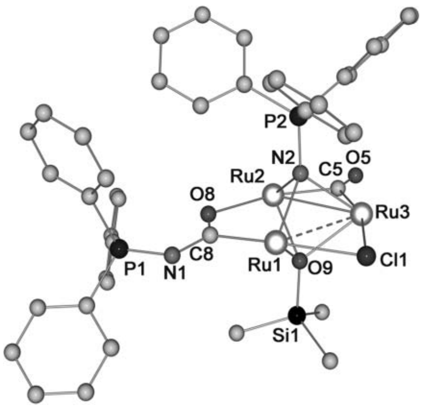
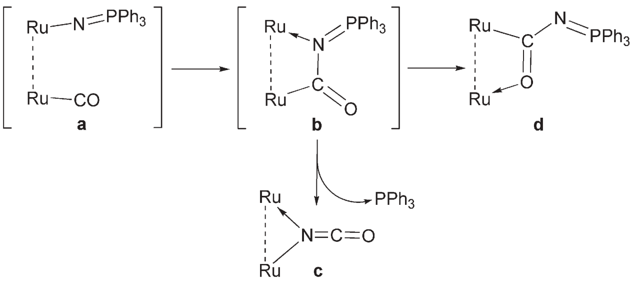


Fig. 2 View of the molecular structure of compound **3** in **3**·0.5CH$_3$OH. The terminal carbonyls (two for each Ru atom) and hydrogens have been omitted for clarity. Selected bond distances (Å) and angles (°): Ru1···Ru2 3.2337(6), Ru1···Ru3 3.1175(7), Ru2–Ru3 2.8627(7), Ru1–Cl1 2.577(1), Ru3–Cl1 2.639(1), Ru2–C5 2.032(4), Ru3–C5 2.048(4), P2–N2 1.613(3), Ru1–N2 2.207(3), Ru2–N2 2.187(3), Ru3–N2 2.208(3), P1–N1 1.611(3), Ru1–C8 2.027(4), Ru2–O8 2.221(2), N1–C8 1.335(4), C8–O8 1.256(4), Ru1–O9 2.174(2), Ru2–O9 2.196(2), Ru3–O9 2.198(2), Si1–O9 1.675(2); Ru2–Ru3–Ru1 65.308(14), C8–N1–P1 123.3(3), O8–C8–N1 123.8(3), O8–C8–Ru1 116.9(2), N1–C8–Ru1 119.2(2), C8–O8–Ru2 118.2(2), Ru1–Cl1–Ru3 73.40(3).

closer to 1, and the P2–N2 distance (1.613(3) Å) is indeed intermediate between that of a single and double bond.

The chloride ligand observed in the crystal structure of cluster **3** probably stems from the pyrolytic reaction of cluster **2** with CH$_2$Cl$_2$, being the only chlorine source in the reaction mixture (note that clusters **1–3** were not observed in the absence of chlorinated solvents). DFT calculations|| were carried out in order to confirm the crystallographic assignment of the oxygen atom in the μ$_3$-OSiMe$_3$ group. Since a NSiMe$_3$ ligand was chemically reasonable and crystallographically possible, a model based on **2** but bearing this group instead of μ$_3$-OSiMe$_3$ was optimized. As qualitatively expected in view of the electron count discussed above, the computation strongly suggests paramagnetic properties (not observed by NMR spectroscopy), with frontier orbitals being occupied by unpaired electrons (see ESI†). To the best of our knowledge, the silanolate group has never previously been reported to μ$_3$-cap metal carbonyl clusters in which it usually behaves as a μ$_2$-ligand.[4] Several examples of capping silanolates on polynuclear compounds with non-bonded transition metal centres have been described.[5] In one case,[6] the ligand OSiMe$_3$ was found to cap a tetranuclear heterocubane, [Cd$_4$I$_4$(μ$_3$-OSiMe$_3$)(μ$_3$-NPEt$_3$)$_3$], formed by the pyrolytic reaction between Et$_3$P=NSiMe$_3$ and CdI$_2$. The presence of the silanolate was explained by the reaction between silicon grease and the intermediate [CdI(NPEt$_3$)]$_4$. Although we tend to rule out a similar hypothesis, since Teflon sealed tubes were used for the reaction, the complicated nature of the radical reactions between CH$_2$Cl$_2$, [Ru$_3$(CO)$_{12}$] and Ph$_3$P=NSiMe$_3$ does not allow an alternative explanation.

The Ph$_3$PNCO ligand could result from the formation of an N–C bond between a coordinated CO and a terminal NPPh$_3$ group, first giving rise to an μ-N,C interaction (intermediate b in Scheme 2).** This would be reminiscent of the formation of organic isocyanates by the carbonylation of nitrene species.[7] At this stage, two alternative pathways are conceivable. The Ph$_3$PNCO group could rearrange to an μ-C,O bonding mode (b → d) or loose PPh$_3$ and form an isocyanate ligand (b → c). Both fragments are present in **2**.



Scheme 2

In order to gain a better insight into the mechanism of these cluster-mediated ligand rearrangements, DFT studies were carried out. Four models were optimized in order to evaluate whether the steric hindrance of the phenyl groups was responsible for the stabilization of the μ-C,O configuration (d). Model compounds **4a** and **4b**, in which the phenyl groups are replaced by hydrogen atoms, were compared to **5a** and **5b** (Fig. 3).

Model **4b** was found to be 8.0 kJ mol^{-1} more stable than **4a**, suggesting that without the steric hindrance of the phenyl groups, the μ-N,C bonding mode would be the preferred one. Optimization of **5a** and **5b** confirmed this hypothesis, with **5a** being now greatly stabilized (39.5 kJ mol^{-1}) with respect to **5b**. If a second Ph$_3$PNCO ligand was bonded to the Ru$_3$ cluster (Scheme 2, b), even in the preferred μ-C,O bonding mode, additional steric hindrance would be generated, especially between the μ$_3$-NPPh$_3$ phenyl groups and those of the two Ph$_3$PNCO ligands. To confirm this hypothesis, calculations were performed on model **6** (Fig. 4), in which the bridging isocyanate ligand of **2** is replaced by a μ-N,C-Ph$_3$NCO group.

Energy minimization resulted in cluster **2** by loss of triphenylphosphine and rearrangement of the remaining fragment to the N-bound isocyanate ligand. A movie obtained rendering the optimization steps is given as supplementary information.†

Thus, pathway a → b → c (Scheme 2) is preferred for the formation and transformation of the second Ph$_3$PNCO group. The b → c sequence can be compared to a classical Hofmann rearrangement, in which a primary amine is formed by oxidation

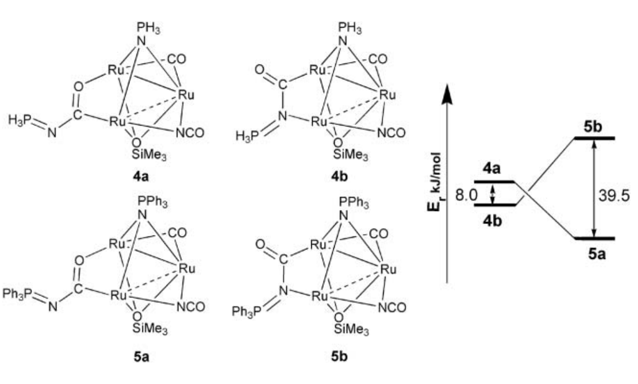


Fig. 3 Structural diagrams of model compounds **4a**, **4b**, **5a** and **5b**, optimized by DFT methods (terminal carbonyls omitted for clarity) and relative energy profiles.

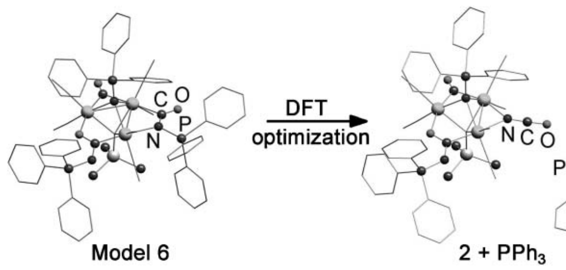
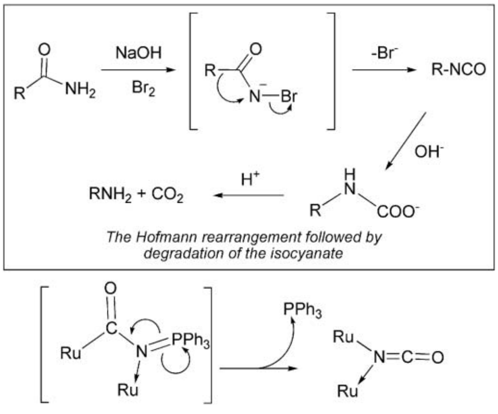


Fig. 4 Views of the input structure for DFT optimization (model **6**) and relative optimized output.



Scheme 3

of an amide (Scheme 3)[8] *via* a seldom isolated isocyanate intermediate. In our case, the generic R group corresponds to a Ru atom, while the oxidation proceeds *via* loss of PPh_3. This mechanism is also somewhat similar to that proposed by Beck and Lindenberg[9] for the rearrangement of hydroxylamine or chloroamine on mononuclear group 6 hexacarbonyls.

In conclusion, we have identified a series of cluster-mediated ligand formation and rearrangement reactions that are reminiscent of the Hofmann rearrangement, and their suggested mechanism was supported by DFT calculations.

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Notes and references

‡ Selected spectroscopic data for **2**: FTIR (pure solid, reflectance, cm^{-1}): ν(μ-NCO) 2177s, ν(μ-CO) 1735m, $\nu(Ph_3PNCO)$ 1433m; ^{31}P NMR (δ, 161.98 MHz, 85% H_3PO_4): 64 (s, μ_3-Ph_3PN), 27 (s, Ph_3PNCO).

§ *Crystal data for* **2** *co-crystallized with* **3**: Formula: $0.4{\cdot}C_{48}H_{39}N_3O_{10}P_2Ru_3Si$, $0.6{\cdot}C_{47}H_{39}N_2ClO_9P_2Ru_3Si$, $M_{av} = 1207.12$, triclinic, space group *P*-1, $a = 11.6159(7)$ $b = 13.3036(7)$, $c = 17.140\ (1)$ Å, $\alpha = 98.473\ (1)$, $\beta = 90.4370(1)$, $\gamma = 104.370(1)°$, $V = 2535.2(3)$ Å^3, $Z = 2$, $D_c = 1.581$ g cm^{-3}, μ(Mo-Kα) = 10.05 mm^{-1}, $F(000) = 1203$. A Bruker SMART1000[10a] diffractometer was employed for the collection of 22509 reflections (Mo-Kα, $\lambda = 0.71073$ Å, $T = 293$ K). The structure was solved by direct methods and refined by a full matrix least-squares technique based on F^2 (SHELXL-97[10b]) with anisotropic thermal parameters. The occupancy factors for the isocyanate group and for the chlorine atom were assigned after analysis of their isotropic thermal parameters. The final R_1 and wR_2 were 0.038 and 0.054, respectively, for 613 parameters and 4879 observed unique reflections ($R_{int} = 0.049$) [$I > 2\sigma(I)$]. CCDC 617271. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b611338a

¶ *Crystal data for* **3**$\cdot 0.5CH_3OH$: $C_{47}H_{39}N_2ClO_9P_2Ru_3Si{\cdot}0.5CH_3OH$, $M = 1220.51$, triclinic, space group *P*-1, $a = 11.608(3)$, $b = 13.277(3)$, $c = 17.196(3)$ Å, $\alpha = 81.920(3)$, $\beta = 89.945(3)$, $\gamma = 76.225(3)°$, $V = 2547(1)$ Å^3, $Z = 2$, $D_c = 1.591$ g cm^{-3}, μ(Mo-Kα) = 10.72 mm^{-1}, $F(000) = 1218$. Identical conditions and techniques to those for the structural work-up of **2** were followed. The collected reflections were 27031, the final R_1 and wR_2 were 0.035 and 0.088, respectively, for 604 parameters and 7729 observed unique reflections ($R_{int} = 0.034$) with [$I > 2\sigma(I)$]. CCDC 617272. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b611338a

|| All calculations were done using the program system TURBOMOLE.[11a] If not mentioned explicitly, we otherwise used the DFT method with the Becke–Perdew functional (BP86).[11b] The Coulomb terms were treated by the RI-J approximation.[11c] We used SV(P) basis sets for the structure optimizations[11d] (single zeta for core orbitals, double zeta for the valence shells and one set of polarization functions for all centres except hydrogen). Single point energies were calculated with larger triple zeta valence plus polarization basis sets (TZVP).[11e]

** Another conceivable mechanism for the formation of the Ph_3PNCO and $OSiMe_3$ ligands could be the reaction of $Ph_3PNSiMe_3$ with CO_2 formed by the pyrolysis of $Ru_3(CO)_{12}$ (traces of homoleptic carbonyl carbide clusters are typically detected as by-products). Since $Ph_3PNSiMe_3$ does not spontaneously react with CO_2, this would have to be a cluster-mediated reaction yielding intermediate b in Scheme 2.

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