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Mixed nitrosyl/phosphinidene and nitrene/phosphinidene clusters of ruthenium†

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Reaction of the aminophosphinidene complex $[Ru_5(CO)_{15}(\mu_4\text{-}PNPr^i_2)]$ 1 with [PPN][NO_2] (PPN = $Ph_3P{=}N{=}PPh_3$) led to the mixed nitrosyl/phosphinidene cluster complex [PPN][$Ru_5(CO)_{13}(\mu\text{-}NO)(\mu_4\text{-}PNPr^i_2)$] 2 which is transformed into the novel nitrene/phosphinidene cluster $[Ru_5(CO)_{10}(\mu\text{-}CO)_2(\mu_3\text{-}CO)(\mu_4\text{-}NH)(\mu_3\text{-}PNPr^i_2)]$ 3 *via* treatment with triflic acid.

Over the past several years we have developed an extensive chemistry based on the transformation of functionalised phosphinidenes on metal clusters including the design of a versatile route to phosphorus monoxide (PO) complexes *via* the acid catalysed hydrolysis of P–N bonds in coordinated aminophosphinidenes.[1] Since PO is the heavier congener of NO while PR and NR ligands are also analogous, we were intrigued by the possibility of generating mixed NO/PO and NR/PR clusters for direct comparison of molecular–electronic structures and bonding[2] of the ligand pairs within single molecules. There are to our knowledge no examples of either type in the literature nor indeed are mixed NO/PR or NR/PO complexes known. In this communication we describe the synthesis, characterisation and transformation of the nitrosyl–phosphinidene cluster [PPN]-[$Ru_5(CO)_{13}(\mu\text{-}NO)(\mu_4\text{-}PNPr^i_2)$] **2** into the nitrene–phosphinidene complex $[Ru_5(CO)_{10}(\mu\text{-}CO)_2(\mu_3\text{-}CO)(\mu_4\text{-}NH)(\mu_3\text{-}PNPr^i_2)]$ **3**.

After attempts to form nitrosyl/phosphinidene clusters using NO gas or nitrosonium tetrafluoroborate failed due to cluster decomposition, we turned to the milder reagent [PPN][NO_2] which is effective in the formation of anionic nitrosyl clusters.[3] Reactions with the nitrite anion occur *via* oxidation of a carbonyl ligand and CO_2 elimination. Thus treatment of the aminophosphinidene complex $[Ru_5(CO)_{15}(\mu_4\text{-}PNPr^i_2)]$ **1** with [PPN][NO_2] led to the anionic nitrosyl/phosphinidene cluster [PPN][$Ru_5(CO)_{13}(\mu\text{-}NO)(\mu_4\text{-}PNPr^i_2)$] **2** in good yield.[4] The IR spectrum of **2** shows a weak band at 1543 cm^{-1}, consistent with the stretching frequency of a doubly bridging nitrosyl ligand.[5] The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at δ 550.7 for the phosphinidene ligand, a downfield shift of more than 60 ppm compared to the starting cluster **1**. Compound **2** has been structurally characterised (Fig. 1).[6] The five ruthenium atoms are arranged in a square-based pyramid. The aminophosphinidene ligand occupies the square face of the pyramid while the nitrosyl ligand bridges one edge of the square base. The nitrosyl bridged Ru–Ru bond distance (2.7077(4) Å) is significantly shorter than the other Ru–Ru distances in the square base (2.8493(4)–2.8986(4) Å). Distances to the apical Ru(5) atom range from 2.8214(4) to 2.8583(4) Å. Thirteen carbonyl ligands are terminally bound to the cluster, two to each of the nitrosyl bound ruthenium atoms and three to each of the other three ruthenium centres. The Ru–N bond lengths to the nitrosyl ligand (Ru(3)–N(9) 1.984(3) Å, Ru(4)–N(9) 2.016(3) Å) indicate a slight asymmetry in the Ru–N–Ru bridge.

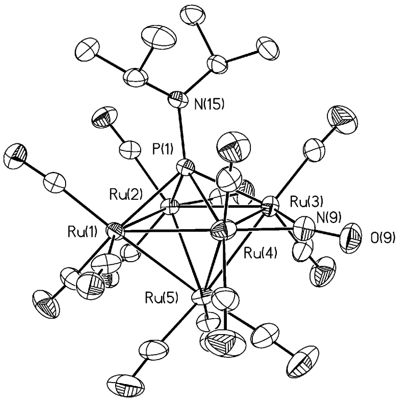

Fig. 1 Molecular structure (ORTEP) of the anion of [PPN][$Ru_5(CO)_{13}(\mu\text{-}NO)(\mu_4\text{-}PNPr^i_2)$] **2**. Hydrogen atoms have been omitted. Thermal ellipsoids are shown at the 50% probability level.

The formation of **2** involves a loss of two carbonyl ligands and coordination of NO in a doubly bridging co–ordination mode as a three-electron donor, resulting in a overall 74 electron count, consistent with a *nido* M_5 structure or a *closo* M_5P framework if the $\mu_4\text{-}PNPr^i_2$ fragment is considered part of the cluster framework. The octahedral metal/phosphinidene core does not change significantly in the reaction. Compound **2** is the first mixed phosphinidene/nitrosyl cluster.

In previous work, we described the acid catalysed hydrolysis of aminophosphinidenes to form PO clusters.[1b] Nitrosyl complexes are also reactive towards acid, undergoing electrophilic attack at oxygen to yield NOH and $NOCH_3$ ligands with H^+ and CH_3^+, respectively.[7] The reactivity of the aminophosphinidene/nitrosyl cluster **2** towards protonation was therefore examined. Treatment of **2** with triflic acid led to the nitrene/phosphinidene cluster $[Ru_5(CO)_{10}(\mu\text{-}CO)_2(\mu_3\text{-}CO)(\mu_4\text{-}NH)(\mu_3\text{-}PNPr^i_2)]$ **3** in moderate yield.[8] The reaction is not affected by added water. The molecular structure of **3** is shown in Fig. 2.[6] The cluster consists of five ruthenium atoms arranged in a square based pyramid with the square face capped by the μ_4-NH

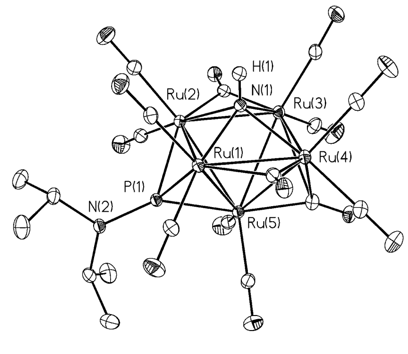

Fig. 2 Structure of $[Ru_5(CO)_{10}(\mu\text{-}CO)_2(\mu_3\text{-}CO)(\mu_3\text{-}PNPr^i_2)(\mu_4\text{-}NH)]$ **3**. Thermal ellipsoids are shown at the 50% level. Hydrogen atoms have been eliminated from the isopropyl groups.

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† Electronic supplementary information (ESI) available: experimental, preparation of compounds. See http://www.rsc.org/suppdata/cc/b1/b110927h

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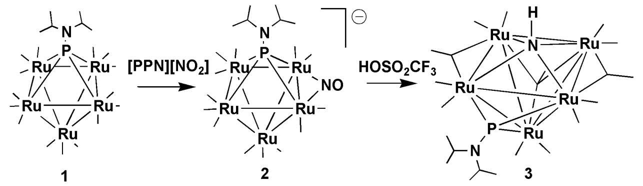
ligand. The Ru–N distances range from 2.136 to 2.158 Å. The hydrogen atom of the nitrene ligand was easily located in a Fourier map and refined. One of the triangular faces of the metal core is bridged by the phosphinidene ligand. The Ru–P distances of 2.2607(5)–2.2839(5) Å are typical for μ_3-phosphinidene ligands.[1a,b,9] The P–N distance of 1.630(1) is slightly shorter than a typical P–N single bond.[10] The cluster contains thirteen carbonyl ligands. One forms a triply bridging interaction at the triangular face opposite to the phosphinidene ligand, while two carbonyls doubly bridge the Ru(2)–Ru(3) and Ru(1)–Ru(4) edges of the square base. The remaining carbonyl ligands are terminal, two on each metal. The Ru–Ru distances for the μ_2-carbonyl-bridged edges are short (2.6929(2) and 2.6978(2) Å). The nitrene and phosphinidene ligands each contribute four electrons, resulting in a cluster electron count of 74e, consistent with the observed electron precise structure.

Complex **3** displays interesting spectroscopic characteristics. The hydrogen atom of the nitrene ligand in **3** appears in the ^{1}H NMR spectrum at δ 3.22 as a 1 : 1 : 1 triplet with coupling to the quadrupolar ^{14}N nucleus (^1J(NH) 50 Hz), presumably due to the symmetric M_4 environment. The ^{31}P chemical shift of δ 495.8 is in the expected range for triply bridging phosphinidene ligands but is shifted upfield from that of the μ_4-phosphinidene in **2** by 55 ppm. The source of the nitrene hydrogen in **3** was investigated by reaction of **2** with triflic acid-d. Deuteration of the nitrene ligand in the resulting product was confirmed by ^{2}H NMR spectroscopy, which shows a broad singlet at δ 3.22 for the ND ligand. Further evidence for the reaction pathway in the conversion of **2** to **3** (Scheme 1) was provided by the mass spectrometric detection of CO_2 in the gas above the reaction mixture,[11] suggesting that CO acts as a reducing agent in the transformation. Since the number of carbonyl ligands in **2** and **3** is the same, cluster decomposition must provide an additional source of CO for coordination. No other cluster species were isolated in the reaction.



Scheme 1

The formation of nitrene (NH) ligands *via* protonation of a nitrosyl ligand was initially observed in the transformation of $\{(\eta^5\text{-}C_5H_4Me)Mn(NO)\}_3(\mu_3\text{-}NO)$ into $\{(\eta^5\text{-}C_5H_4Me)Mn(NO)\}_3(\mu_3\text{-}NH)$.[12] The present work is of interest because it is the first example of the transformation of a μ-NO ligand to a μ_4-NH ligand. Quadruply bridging NH ligands are relatively rare but have been produced by protonation of nitrides,[13] or *via* thermolysis or hydrogenation of $NOCH_3$ ligands.[14] Also of note in the reaction is the apparent preference for a quadruply bridging nitrene ligand, requiring that the μ_4-phosphinidene ligand of the starting cluster move into a μ_3-coordination mode.

In conclusion, we have synthesised the first examples of mixed nitrosyl–phosphinidene and nitrene–phosphinidene clusters. Our results suggest that μ-NO ligands in these Ru_5 systems are more susceptible to electrophilic attack (H^+ addition) than are μ_4-$PNPr^i_2$ groups, giving preferential conversion of NO to NH ligands over $PNPr^i_2$ to PO.

We are currently exploring the generation of μ_n-NO ligands on preformed PO clusters and the comparative chemistry of the four NO–PO–PR–NR combinations.

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4 *Data* for $[PPN][Ru_5(CO)_{13}(\mu\text{-}NO)(\mu_4\text{-}PNPr^i_2)]$ **2**: IR (CH_2Cl_2 soln), ν(CO): 2053m, 2005vs, 1987s, 1949vw, 1925(sh), ν(NO): 1543w. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 550.7 (s, $PNPr^i_2$), 21.7 (s, PPN). ^{1}H NMR: δ 7.5 (m, PPN), 3.85 (sept, 2H, CH), 1.15 (d, 12H, CH_3). FAB–MS (*m*/*z*): 1031 $[M]^-$, 1003–947 $[M - n\text{CO}]^-$ (n = 1–3).

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6 *Crystal data*: for $[PPN][Ru_5(CO)_{13}(\mu\text{-}NO)(\mu_4\text{-}PNPr^i_2)]$ **2**: M = 1569.19, triclinic, $P\bar{1}$, a = 11.0845(7), b = 16.4630(1), c = 16.7626(1), α = 101.7430(1) Å, β = 102.5560(1), γ = 97.3690(1)°, V, = 2875.2(3) Å^3, Z = 2, μ(Mo-Kα) = 1.433 mm^{-1}, R [$I > 2\sigma(I)$] = 0.0351, $wR2$, (all data) = 0.0855, 14739 data, 721 parameters. For $[Ru_5(CO)_{10}(\mu\text{-}CO)_2(\mu_3\text{-}CO)(\mu_4\text{-}NH)(\mu_3\text{-}PNPr^i_2)]\cdot CH_2Cl_2$ **3**: M = 1100.58, monoclinic, $P2_1/c$, a = 13.4582(7), b = 12.9073(7), c = 19.465(1) Å, β = 109.780(1)°, V = 3181.8(3) Å^3, Z = 4, μ(Mo-Kα) = 2.598 mm^{-1}, R [$I > 2\sigma(I)$] = 0.0182, $wR2$ (all data) = 0.0432, 8224 data, 402 parameters. CCDC reference numbers 176891 and 176892. See http://www.rsc.org/suppdata/cc/b1/b110927h/ for crystallographic data in CIF or other electronic format.

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8 *Data* for $[Ru_5(CO)_{10}(\mu\text{-}CO)_2(\mu_3\text{-}CO)(\mu_4\text{-}NH)(\mu_3\text{-}PNPr^i_2)]$ **3**. IR (CH_2Cl_2 soln), ν(NH): 3319s, ν(CO): 2076w, 2033vs, 1995m, 1855br. $^{31}P\{^1H\}$ NMR: δ 495.8. ^{1}H NMR: δ 4.76 (sept., ^3J(HH) 6.8 Hz, CH), 3.22 (1 : 1 : 1 triplet, $^1J(^{14}NH)$ 50 Hz), 1.71 (d, ^3J(HH) 6.8 Hz, CH_3). ^{2}H NMR: δ 3.22 (br). Anal. Calc. for $C_{19}H_{15}O_{13}PN_2$: C, 22.47; H, 1.49; N, 2.76. Found: C, 22.14; H, 1.31; N, 2.79%.

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