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Hexaruthenium cluster complexes of basal edge-bridged square pyramidal metallic skeleton. First efficient synthesis and reactivity studies†

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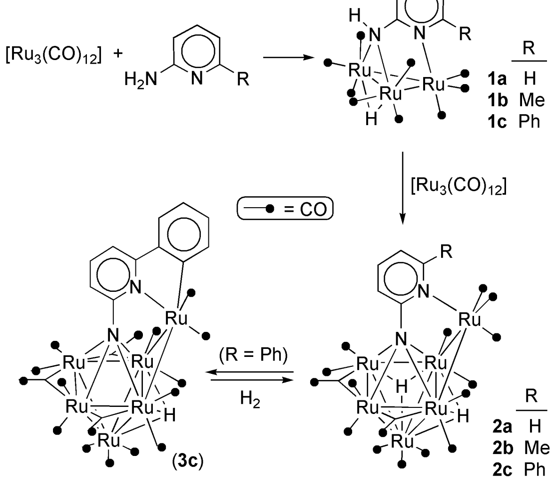
An easy one-pot synthetic procedure has led to the first high-yield preparation of hexanuclear cluster complexes of a so far uncommon metallic skeleton, basal edge-bridged square pyramid, directly from the easily available starting materials $[Ru_3(CO)_{12}]$ and 2-aminopyridines. This efficient synthesis has opened up the possibility of studying the hitherto unexplored reactivity of these cluster complexes.

During the last 40 years, many efforts have been devoted to prepare transition metal carbonyl cluster complexes in rational and systematic ways.[1] However, to date, no efficient syntheses of hexanuclear complexes containing a basal edge-bridged square pyramidal metallic skeleton have been reported. This has made it difficult to study their reactivity and their catalytic activity as precursors for the transformation of organic substrates. The few hexaruthenium cluster complexes of this type that have been reported have been prepared in several steps from $[Ru_3(CO)_{12}]$ in low overall yields.[2–4]

We describe herein the first easy, one-pot, and high-yield transformation of $[Ru_3(CO)_{12}]$ into hexaruthenium cluster complexes with a basal edge-bridged square pyramidal metallic skeleton. We also report some preliminary reactivity results.

Treatment of $[Ru_3(CO)_{12}]$ with half equiv. of 2-aminopyridine (H_2apyH) in refluxing xylene (mixture of isomers) for 1 h allowed the isolation of the hexanuclear cluster $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-apyH})(\mu\text{-}CO)_2(CO)_{14}]$ (**2a**) in 70 % yield (Scheme 1).[5a]



Scheme 1

Interestingly, while the use of 2-amino-6-methylpyridine (H_2apyMe) led to the analogous $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-apyMe})(\mu\text{-}CO)_2(CO)_{14}]$ (**2b**) in 77 % yield,[5b] the use of 2-amino-6-phenylpyridine (H_2apyPh) afforded a mixture of $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-apyPh})(\mu\text{-}CO)_2(CO)_{14}]$ (**2c**)[5c] and the orthometalated derivative $[Ru_6(\mu_3\text{-}H)(\mu_5\text{-}\eta^3\text{-apy}C_6H_4)(\mu\text{-}CO)_3(CO)_{13}]$ (**3c**).[6] By monitoring the reactions by IR and spot TLC, it was observed that the trinuclear derivatives $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-HapyR})(CO)_9]$ (**1a**–**c**)[7] are early intermediates (they appeared after the first 5 min) in the formation of complexes **2a**–**c**. In fact, in subsequent experiments we proved that **2a**–**c** can also be made by reacting **1a**–**c** with one equiv. of $[Ru_3(CO)_{12}]$ in refluxing xylene for 1 h. The driving force for these reactions appears to be the marked tendency of the bridgehead amido group to undergo N–H bond activation to give a nitrene, the latter serving as a capping unit that holds four metal atoms together.

Complex **3c** reacted with hydrogen (slow bubbling, THF, reflux temperature, 1 h) to give **2c** in quantitative yield. However, the thermolysis of **2c** in refluxing xylene gave only a small amount of the cyclometalated derivative **3c** (among other unidentified products) even after long reaction times (3 h).

The structures of compounds **2c**[8] and **3c**,[9] as representative examples of the hexanuclear compounds depicted in Scheme 1, were confirmed by X-ray diffraction methods. The structure of **2c** is comparable to that reported for $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-}NCO_2Me)(\mu\text{-}CO)_2(CO)_{14}]$ (reported yield: 5%), in which the N atom caps the metallic square and the carbonyl oxygen atom is attached to the Ru atom that bridges the edge of the square pyramid.[4] These compounds are rare examples of complexes having μ_4-NR fragments.[4,10]

The successful synthesis of complexes **2a**–**c** enabled us to undertake a general study of the reactivity of this class of compounds. We chose compound **2b** as an appropriate starting material because the presence of the methyl group on the pyridine ring facilitates the monitoring of the reactions by NMR spectroscopy. In addition, the use of HapyMe as face-capping ligand in triruthenium complexes (such as **1b**) has already allowed an extensive derivative chemistry.[11]

As reactivity studies on carbonylmetal clusters with such a metallic skeleton were unprecedented, their reactive coordination sites, *i.e.* the metal atoms that are prone to undergo nucleophilic addition or substitution processes, were also unknown. This has now been ascertained by studying the reactions of **2b** with triphenylphosphane and the borohydride anion.

The reaction of **2b** with triphenylphosphane occurred readily (THF, reflux temperature, 10 min) to give, initially, a mixture of two isomeric monosubstituted products, in a 5 : 1 mole ratio, which were not separated.[12] Both reacted with more triphenylphosphane (1,2-dichloroethane, reflux temperature, 50 min) to give the disubstituted derivative $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-apyMe})(\mu\text{-}CO)_2(CO)_{12}(PPh_3)_2]$ (**4b**).[13] Therefore, the monosubstituted

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† Electronic supplementary information (ESI) available: synthetic procedures and complete spectroscopic and analytical data for all new compounds; experimental details for measurement and refinement of X-ray diffraction data and ORTEP representations for compounds **2c**, **3c**, **4b**, and **5b**. See http://www.rsc.org/suppdata/dt/b3/b305551e/

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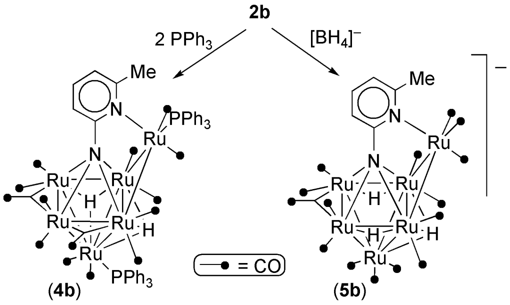
intermediates most probably have their phosphane ligands in the same positions as **4b** (Scheme 2), the structure of which was determined by X-ray diffraction.[14] Thus, the most reactive sites of these hexanuclear clusters (**2a**–**c**) in substitution processes with phosphane ligands have been shown to be the vertex atom of the square pyramid and the edge-bridging ruthenium atom.



Scheme 2

Another interesting reaction is that of **2b** with [PPN][BH_4], which occurred instantaneously in dichloromethane at room temperature and gave [PPN][$Ru_6(\mu_3\text{-H})(\mu\text{-H})_2(\mu_5\text{-}\eta^2\text{-apyMe})(\mu\text{-CO})(CO)_{14}$] (**5b**) (Scheme 2).[15] Its ^{1}H NMR spectrum and its X-ray structure[16] indicated the substitution of a hydride for a carbonyl ligand. Although the hydride ligands of **5b** were not located by Fourier difference mapping, potential energy calculations using XHYDEX[17] indicated that one is face-capping and two are edge-bridging, as shown in Scheme 2. Thus, the incoming hydride ligand substitutes a bridging carbonyl ligand.

No reaction was observed when **2b** was treated with an excess of tetrafluoroboric acid in dichloromethane.

The 2-aminopyridine-derived ligands are not innocent in this chemistry, on the contrary, they play important roles, such as: (a) promoting the formation of the basal edge-bridged square pyramidal metallic skeleton, (b) they help maintain this metallic framework during the reactions of their derivatives, preventing cluster degradation, and (c) as they are hard ligands, they facilitate carbonyl substitution processes, that take place under mild conditions.

In summary, we have communicated herein the first high-yield synthesis of hexanuclear carbonylruthenium clusters having a basal edge-bridged square pyramidal metallic framework. Preliminary reactivity studies have shown that these complexes undergo easy carbonyl substitution processes not only with π-acceptor ligands, such as triphenylphosphane, but also with hard σ-donors, like the hydride anion.

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5 The isostructural compounds **2a**–**c** have comparable spectroscopic data: (*a*) For **2a**: IR (CH_2Cl_2): ν(CO) = 2095 (m), 2071 (s), 2049 (s), 2033 (vs), 2019 (s, sh), 1996 (m, sh), 1973 (m, br), 1954 (w, sh), 1861 (w, br), 1828 (w, br) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 293 K): δ = 7.77 (dd, J = 5.5, 1.4 Hz, 1 H), 7.22 (ddd, J = 8.7, 7.2, 1.4 Hz, 1 H), 6.59 (ddd, J = 7.2, 5.5, 1.1 Hz, 1 H), 5.77 (d, br, J = 8.7 Hz, 1 H), −11.73 (d, J = 2.4 Hz, 1 H), −16.04 (d, J = 2.4 Hz, 1 H); (*b*) For **2b**: IR (CH_2Cl_2): ν(CO) = 2094 (m), 2068 (s), 2049 (s), 2033 (vs), 2014 (m), 1995 (w, sh), 1973 (m, br), 1954 (w, sh), 1860 (w, br), 1828 (w, br) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 293 K): δ = 7.21 (t, J = 7.8 Hz, 1 H), 6.64 (d, J = 7.8 Hz, 1 H), 5.76 (d, J = 7.8 Hz, 1 H), 2,56 (s, 3 H), −11.46 (d, J = 2.2 Hz, 1 H), −15.90 (d, J = 2.2 Hz, 1 H); (*c*) For **2c**: IR (CH_2Cl_2): ν(CO) = 2094 (m), 2069 (s), 2048 (s), 2032 (vs), 2013 (m, sh), 1994 (w, sh), 1972 (m), 1951 (w, sh), 1859 (m, br), 1827 (m, br) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 293 K): δ = 7.57–7.48 (m, 3 H), 7.32 (dd, J = 8.3, 7.5 Hz, 1 H), 7.20 (d, br, J = 7.1 Hz, 1 H), 7.11 (d, br, J = 7.5 Hz, 1 H), 6.62 (dd, J = 7.1, 1.2 Hz, 1 H), 5.90 (dd, J = 8.3, 1.2 Hz, 1 H), −11.46 (d, J = 2.4 Hz, 1 H), −15.87 (d, J = 2.4 Hz, 1 H).

6 Spectroscopic data for **3c**: IR (CH_2Cl_2): ν(CO) = 2088 (m), 2050 (vs), 2028 (m), 2014 (m), 1997 (w, sh), 1961 (w, sh), 1880 (w), 1860 (m), 1841 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 293 K): δ = 7.85 (dd, J = 7.5, 0.8 Hz, 1 H), 7.64 (dd, J = 7.9, 1.6 Hz, 1 H), 7.39 (td, J = 7.5, 1.6 Hz, 1 H), 7.24–7.13 (m, 3 H), 5.15 (d, J = 7.1 Hz, 1 H), −11.62 (s, br, 1 H).

7 (*a*) Compounds **1a** and **1b** have been reported previously: P. L. Andreu, J. A. Cabeza, V. Riera, Y. Jeannin and D. Miguel, *J. Chem. Soc., Dalton Trans.*, 1990, 2201; (*b*) Spectroscopic data for **1c**: IR (CH_2Cl_2): ν(CO) = 2079 (m), 2050 (s), 2026 (vs), 1997 (s), 1987 (m), 1961 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 293 K): δ = 7.60–7.49 (m, 3 H), 7.51 (t, J = 7.7 Hz, 1 H), 7.34–7.30 (m, 2 H), 6.79 (dd, J = 7.7, 1.2 Hz, 1 H), 6.61 (dd, J = 7.7, 1.2 Hz, 1 H), 4.68 (s, br, 1 H), −11.25 (s, 1 H).

8 Selected crystal and refinement data for **2c**·$(CH_2Cl_2)_{0.5}$: $C_{27}H_{10}N_2O_{16}Ru_6 \cdot 0.5(CH_2Cl_2)$, M = 1267.25, monoclinic, $P2_1/c$, dark brown, a = 11.8240(3) Å, b = 15.0404(4) Å, c = 19.4733(5) Å, β = 95.778(2)°, T = 120(2) K, Z = 4, collected/unique reflections 33790/6283 (R_{int} = 0.054), R_1 = 0.0304. CCDC reference number 207015. See http://www.rsc.org/suppdata/dt/b3/b305551e/ for crystallographic data in CIF or other electronic format.

9 Selected crystal and refinement data for **3c**: $C_{27}H_8N_2O_{16}Ru_6$, M = 1222.77, monoclinic, $P2_1/c$, dark green, a = 10.1497(3) Å, b = 10.6673(3) Å, c = 30.1217(9) Å, β = 92.410(2)°, T = 120(2) K, Z = 4, collected/unique reflections 65586/5973 (R_{int} = 0.045), R_1 = 0.0450. CCDC reference number 207014. See http://www.rsc.org/suppdata/dt/b3/b305551e/ for crystallographic data in CIF or other electronic format.

10 For examples of metal clusters having μ_4-NR ligands, see: (*a*) J. A. Cabeza, I. del Río, S. García-Granda, M. Moreno, V. Riera, M. J. Rosales-Hoz and M. Suárez, *Eur. J. Inorg. Chem.*, 2001, 2899 and references cited therein; (*b*) E. N. M. Ho and W. T. Wong, *J. Chem. Soc., Dalton Trans.*, 1998, 4215; (*c*) J. Scoles, B. T. Sterenberg, K. A. Udachin and A. J. Carty, *Chem. Commun.*, 2002, 320.

11 For reactivity studies on Ru_3 clusters containing deprotonated 2-aminopyridines, see: (*a*) J. A. Cabeza, *Eur. J. Inorg. Chem.*, 2002, 1559 (review); (*b*) J. A. Cabeza, I. del Río, S. García-Granda, V. Riera and M. Suárez, *Organometallics*, 2002, **21**, 5005; (*c*) J. A. Cabeza, I. del Río, S. García-Granda, L. Martínez-Méndez, M. Moreno and V. Riera, *Organometallics*, 2003, **22**, 1164.

12 Selected NMR data for the mixture of isomers: (*a*) Major isomer: ^{1}H NMR ($CDCl_3$, 293 K): δ = −11.66 (dd, J = 6.4, 2.0 Hz, 1 H), −15.18 (t, J = 2.0 Hz, 1 H); ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K): δ = 23.21 (s); (*b*) Minor isomer: ^{1}H NMR ($CDCl_3$, 293 K): δ = −11.50 (s, br, 1 H), −13.52 (s, br, 1 H); ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K): δ = 36.98 (s, br).

13 Spectroscopic data for **4b**: IR (CH_2Cl_2): ν(CO) = 2068 (vw), 2053 (m), 2024 (vs), 2011 (vs), 1998 (m, sh), 1981 (w, sh), 1957 (m, br), 1933 (w, sh), 1841 (w, br), 1806 (w, br) cm^{-1}. ^{1}H NMR ($CDCl_3$, 293 K): δ = 7.90–6.80 (m, 31 H), 6.26 (d, J = 7.6 Hz, 1 H), 5.59 (d, J = 7.6 Hz, 1 H), 1.95 (s, 3 H), −11.45 (m, 1 H), −14.08 (m, 1 H). ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K): δ = 41.2 (s, 1 P), 20.7 (s, 1 P).

14 Selected crystal and refinement data for **4b**: $C_{56}H_{38}N_2O_{14}P_2Ru_6$, M = 1631.24, triclinic, P-1, dark red, a = 13.4886(4) Å, b = 14.8157(4) Å, c = 18.3555(5) Å, α = 69.068(2)°, β = 74.458(2)°, γ = 63.290(2)°, T = 200(2) K, Z = 2, collected/unique reflections 80528/11107 (R_{int} = 0.067), R_1 = 0.0648. CCDC reference number 207016. See http://www.rsc.org/suppdata/dt/b3/b305551e/ for crystallographic data in CIF or other electronic format.

15 Spectroscopic data for **5b**: IR (CH_2Cl_2): ν(CO) = 2064 (m), 2033 (s), 1999 (vs), 1974 (m, sh), 1937 (m, br), 1777 (w, br) cm^{-1}. ^{1}H NMR ($CDCl_3$, 293 K): δ = 7.90–7.30 (m, 30 H), 6.89, (t, J = 7.9 Hz, 1 H), 6.24 (d, J = 7.9 Hz, 1 H), 6.01 (d, J = 7.9 Hz, 1 H), 2.42 (s, 3 H), −9.28 (s, 2 H), −15.53 (s, 1 H).

16 Selected crystal and refinement data for **5b**: $C_{57}H_{39}N_3O_{15}P_2Ru_6$, M = 1674.27, triclinic, P-1, dark green, a = 11.7624(4) Å, b = 15.2986(6) Å, c = 17.4724(7) Å, α = 108.457(2)°, β = 94.069(3)°, γ = 96.956(2)°, T = 120(2) K, Z = 2, collected/unique reflections 19079/10736 (R_{int} = 0.050), R_1 = 0.0508. CCDC reference number 207017. See http://www.rsc.org/suppdata/dt/b3/b305551e/ for crystallographic data in CIF or other electronic format.

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