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Preliminary communication

Selective carbonyl substitution reactions on $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(CO)_9]$ and on its protonated derivative. Crystal structure of $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_9][BF_4]$ (Hampy = 2-amino-6-methylpyridine)

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Abstract

The reactions of $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(CO)_9]$ (**1**) (Hampy = 2-amino-6-methylpyridine) with PPh_3 or dppm lead to replacement of one or two of the equatorial CO ligands that are *cis* to the bridging NH fragment and *cis* to the hydride. In contrast, the reactions of the protonated derivative $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_9][BF_4]$ (**2**) with PPh_3 or dppm involve replacement of equatorial CO ligands only on the ruthenium atoms bonded to one hydride ligand.

Carbonyl substitutions on nonacarbonyltriruthenium clusters containing ligands other than phosphines and phosphites have been very little studied [1]. Use of P-donor ligands (L) in the thermal [2 *], photochemical [2] or redox-promoted [3] substitution of CO groups on $[Ru_3(CO)_{12}]$ generally leads to $[Ru_3(CO)_{12-n}(L)_n]$ ($n = 1$–3), but substitution products in which $n > 3$ have been obtained only under forcing conditions with small [4] or chelating [5] P-donor ligands.

Since N-donor ligands are harder, and therefore better *cis*-labilizers, than P-donor ligands in non-cluster complexes [6], we decided to investigate the carbonyl substitu-

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* Reference number with asterisk indicates a note in the list of references.

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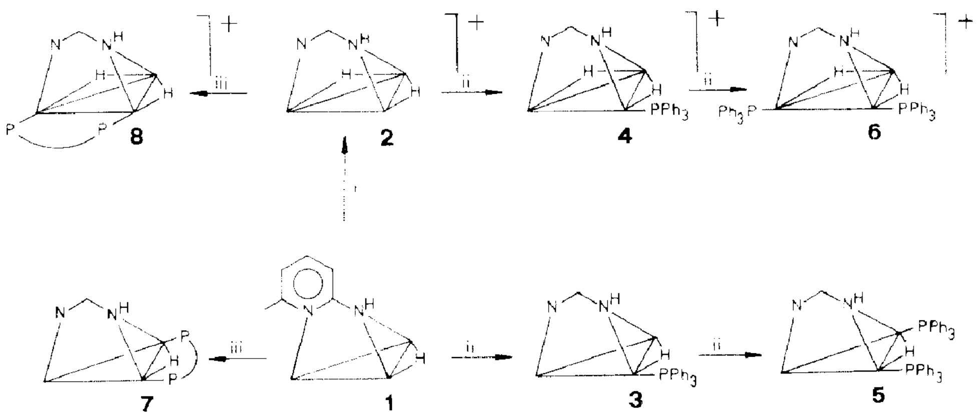

Scheme 1. Reagents: (i) $HBF_4 \cdot OEt_2$, (ii) PPh_3, (iii) dppm.

tion reactions of the nonacarbonyl cluster $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(CO)_9]$ (**1**) [7 *] and its protonated derivative $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_9][BF_4]$ (**2**) (Hampy = 2-amino-6-methylpyridine), which have the three ruthenium atoms attached to nitrogen [8 *].

Complex **1** is readily protonated by $HBF_4 \cdot OEt_2$ in dichloromethane to give the cationic complex **2*** (Scheme 1). The crystal structure ** of **2** (Fig. 1) shows that one hydride ligand bridges the edge of the triangle that is also spanned by the NH fragment, while the other hydride bridges one of the other two edges. When **1** and **2** are treated with an excess of PPh_3 in THF solution at room temperature, complexes **3** and **4** are readily formed. In both cases the displaced CO was that *cis* to the NH fragment and *cis* to the hydride, as inferred from the low *J*(P–hydride) coupling constants (Table 1) and from the fact that the amido group is more *cis*-labilizing than pyridine. The ^1H NMR spectrum of complex **4** also confirms that the PPh_3 ligand is not attached to the ruthenium bonded to the two hydrides, since one of the two *J*(P–hydride) coupling constants is very small (2.8 Hz).

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* All the isolated yields were always higher than 60%. All compounds gave satisfactory microanalysis (C, H, N). IR data (cm^{-1}): ν(CO): **2** (THF): 2139m, 2101s, 2087s, 2076s, 2064m, 2039m, 2026s, 1966w; **3** (THF): 2058m, 2020s, 1992m, 1979m, 1958m, 1939w; **4** (THF): 2133m, 2081s, 2054m, 2028m, 2010m, 1957w; **5** (THF): 2030m, 1992s, 1974w, 1958s, 1939w, 1926w; **6** (CH_2Cl_2): 2122w, 2058m, 2033s, 2002m, 1970m, 1950w; **7** (THF): 2031s, 1988s, 1975w, 1955s, 1935w, 1926w; **8** (CH_2Cl_2): 2124s, 2067s, 2049s, 2026s, 2005s, 1970m, 1951w. ν(NH) (Nujol mull): **2**: 3280m, **3**: 3284w; **4**: 3283m; **5**: 3292w; **6**: 3266w; **7**: 3309w; **8**: 3300m. Table 1 lists some selected NMR data.

** Crystal data for **2**: $C_{15}H_9BF_4N_2O_9Ru_3$, $M = 751.3$, monoclinic, space group $C2/c$, a 23.468(6), b 15.524(6), c 15.283(3) Å, β 122.83(2)°, V 4679(2) Å^3, $Z = 8$, $D_c = 2.13$, $F(000) = 2864$, λ 0.71069 Å, $\mu(\text{Mo-}K_\alpha)$ 19.54 cm^{-1}. The intensities of 3515 reflections were collected on a CAD-4 Enraf-Nonius diffractometer ($1.5 < \theta < 25°$, scan width $1.20 + 0.34 \tan \theta$) using the $\omega-2\theta$ mode and Mo-K_α radiation (graphite monocromator). 2872 reflections with $F > 3\sigma(F)$ were used in the refinement. Two standard reflections examined every 2 h showed no change. Absorption correction was made by an empirical method based on the ψ-scan of one reflection (minimum–maximum transmission factor 1.00–1.25). The structure was solved by direct methods and subsequent Fourier maps and refined by least squares in three blocks (337 parameters) with anisotropic thermal parameters for the non-hydrogen atoms. All hydrogen atoms were located from difference maps and were given an isotropic overall thermal parameter. Correction was made for anomalous dispersion. A secondary extinction correction was made. Final R and R_w values were 0.0248 and 0.0269. The atomic coordinates and a complete list of bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre.

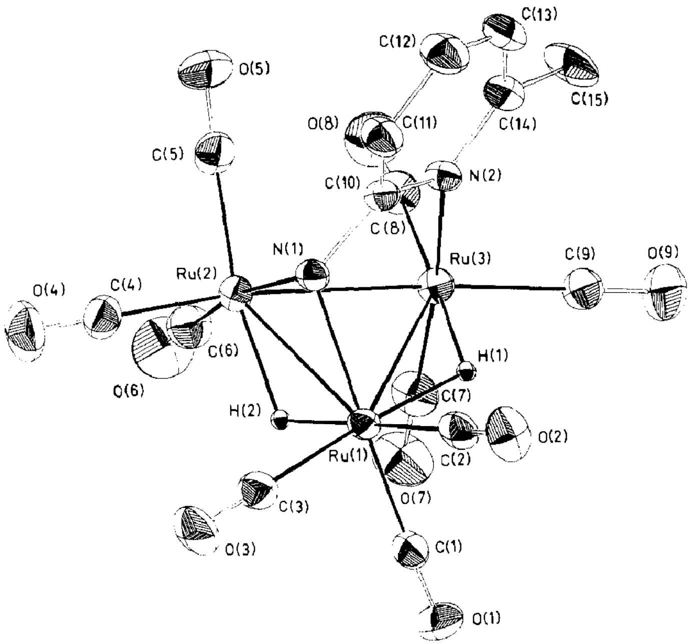

Fig. 1. Perspective view of the cation $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_9]^+$ (**2**). Selected bond lengths (Å) and angles (°): Ru(1)–Ru(2) 2.7855(5), Ru(1)–Ru(3) 2.9426(5), Ru(2)–Ru(3) 2.7437(5), Ru(1)–H(1) 1.70(6), Ru(1)–H(2) 1.75(6), Ru(2)–H(2) 1.80(6), Ru(3)H(1) 1.74(6), Ru(1)–N(1) 2.106(3), Ru(2)–N(1) 2.098(4), Ru(3)–N(2) 2.177(4); Ru(3)–Ru(1)–Ru(2) 57.16(1), Ru(3)–Ru(2)–Ru(1) 64.30(1), Ru(2)–Ru(3)–Ru(1) 58.54(1), Ru(3)–H(1)–Ru(1) 117.6(33), Ru(2)–H(2)–Ru(1) 103.4(30), Ru(2)–N(1)–Ru(1) 83.0(1).

Although complexes **3** and **4** do not react further with PPh_3 at room temperature, they give the disubstituted compounds **5** and **6** in refluxing THF, with no evidence for formation of trisubstituted complexes, even after prolonged reflux with a large excess of PPh_3. As expected, the hydride resonance of **5** appears as a triplet, and the $^{31}P(^1H)$ MNR spectrum consists of a singlet. In complex **6**, the low values of the

Table 1

Selected NMR data [a]

Compound	^1H NMR [b]			$^{31}P\{^1H\}$ NMR	
	δ (ppm)	J(HH) (Hz)	J(HP) (Hz)	δ (ppm)	J(PP) (Hz)
2	−13.37(d)	3.2			
	−14.74(d)	3.2			
3	−11.10(d)		9.2	35.61(s)	
4	−13.14(t)	2.8	2.8	28.82(s)	
	−14.15(dd)	2.8	18.3		
5	−9.91(t)		8.3	31.32(s)	
6	−12.91(dt)	4.0	2.0, 2.0	30.25(d)	49.3
	−13.33(ddd)	4.0	13.3, 2.0	26.38(d)	49.3
7	−10.84(td)	4.5 [c]	13.4	2.62(s)	
8	−12.41(ddd)	2.5	25.0, 1.0	21.49(d)	36.4
	−14.12(ddd)	2.5	25.0, 1.0	14.89(d)	36.4

[a] Spectra recorded at 20 °C, in $CDCl_3$, on a Bruker AC-300 instrument. [b] Hydride region only. [c] N*H*-hydride coupling.

J(P–hydride) coupling constants and the large J(P–P) coupling in the ^{31}P(^{1}H) NMR spectrum indicate that both PPh_3 ligands are *cis* to hydride and mutually *trans* on the same edge of the triangle, ruling out the possibility that there could be one PPh_3 on the ruthenium bonded to the two hydrides.

The reactions of **1** and **2** with dppm take place at room temperature in THF to give the complexes 7 (which is similar to **5**) and **8**, respectively. The hydride signal from **7** is a triplet of doublets, this being the only example in which coupling of the hydride to the N*H* is observed. In the case of complex **8**, the small bite of the dppm ligand forces its coordination to be *trans* to the hydrides. This is confirmed by the large J(P–H) couplings.

It is apparent that the *cis*-labilizing effects of the 2-aminopyridinate and hydride ligands favour the displacement of CO groups from specific sites in triruthenium nona- and octa-carbonyl clusters under very mild conditions. We expect that the observations described above will lead to a variety of ruthenium clusters which will show a range of chemical and catalytic properties arising from different combinations of bridging and terminal ligands. Further work in this area is in progress.

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References

1 (a) M.I. Bruce, M.G. Humphrey, O.B. Shawkataly, M.R. Snow and E.R.T. Tiekink, J. Organomet. Chem., 336 (1897) 199; (b) C. Jangala, E. Rosemberg, D. Skinner, S. Aime, L. Milone and E. Sappa, Inorg. Chem., 19 (1980) 1571; M.I. Bruce, M.A. Cairns and M. Green, J. Chem. Soc., Dalton Trans., (1972) 1293.

2 For a general review on substitution reactions on [$Ru_3(CO)_{12}$] see, M.I. Bruce in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon, London 1982, Vol. IV, p. 872.

3 M.I. Bruce, Coord. Chem. Rev., 76 (1987) 1.

4 M.I. Bruce, G. Shaw and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1972) 2094; M.I. Bruce, J.G. Matisons and B.K. Nicholson, J. Organomet. Chem., 247 (1983) 321.

5 D.W. Engel, K.G. Moodley, L. Subramony and R.J. Haines, J. Organomet. Chem., 349 (1983) 393; W.R. Cullen and D.A. Hardbone, Inorg. Chem., 9 (1970) 1839; S. Cartwright, J.A. Clucas, R.H. Dawson, D.J. Foster, M.M. Harding and A.K. Smith, J. Organomet. Chem., 302 (1986) 403; J.A. Clucas, D.J. Foster, M.M. Harding and A.K. Smith, J. Chem. Soc., Dalton Trans., (1987) 277; D.A. Brandes and R.J. Puddephatt, Inorg. Chim. Acta, 113 (1986) 17; J.A. Cabeza, V. Riera, Y. Jeannin and D. Miguel, ibid., in press.

6 J.D. Atwood and T.L. Brown, J. Am. Chem. Soc., 98 (1976) 3155.

7 The synthesis of complex **1** and the X-ray structure of the analogous cluster [$Ru_3(\mu$-H)(μ_3-2-anilinopyridinate)$(CO)_9$] have been reported: P.L. Andreu, J.A. Cabeza, V. Riera, Y. Jeannin and D. Miguel, submitted for publication.

8 It is noteworthy that very few nonacarbonyltriruthenium clusters containing triply-bridging N-donor ligands have been published: Ref. 1(a); Ref. 7; J.A. Smieja, J.E. Gozum and W.L. Gladfelter, Organometallics, 5 (1986) 2154; S.H. Han and G.L. Geoffrey, Polyhedron, 7 (1988) 2331; D.P. Maddern, A.J. Carty and T. Birchall, Inorg. Chem., 11 (1972) 1453; P. Mastropasqua, P. Lahuerta, K. Hildebrand and H. Kisch, J. Organomet. Chem., 172 (1979) 57; J.A. Cabeza, L.A. Oro, A. Tiripicchio and M. Tiripicchio-Camellini, J. Chem. Soc., Dalton Trans., (1988) 1437. S.H. Han, J.S. Song, P.D. Macklin, S.T. Nguyen, G.L. Geoffroy and A.L. Rheingold, Organometallics, 8 (1989) 2270.