Notes

Reaction of Triruthenium Dodecacarbonyl with Nitrobenzene and Structure of μ_3-Phenylnitrene-triruthenium Decacarbonyl, $[Ru_3(CO)_{10}(\mu_3\text{-}NPh)]$ †

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Triruthenium dodecacarbonyl $[Ru_3(CO)_{12}]$ reacts with nitrobenzene to give $[Ru_3(CO)_{10}(NPh)]$ (3) and $[Ru_3(CO)_9(NPh)_2]$ (4) in low yields, accompanied by formation of CO_2. The solution i.r. spectrum of (3) suggests the presence of triply bridging NPh and CO groups, confirmed by a single-crystal *X*-ray structure determination: space group $P2_1/n$, $a = 12.457(1)$, $b = 11.428(1)$, $c = 29.234(2)$ Å, $\beta = 92.38(1)°$, $Z = 8$, and $R = 0.036$ for 4 817 unique observed reflections. The two independent molecules differ slightly in the relative orientations of the phenyl groups. Mean bond lengths include Ru–Ru 2.746(5), Ru–μ-C 2.172(8), and Ru–μ-N 2.055(5) Å. The i.r. spectra of complexes (3) and (4) are discussed in terms of a molecular-orbital description of '$M_3(CO)_9$' moieties.

Involvement of nitrene intermediates has been proposed in catalytic reactions where nitrobenzene is one of the reactants.[1] Recently, polynuclear metal carbonyls have been used as catalysts in the conversion of nitrobenzene into aniline.[2] Isolation of polynuclear complexes with 'PhN' groups interacting with more than one metal atom could be taken as indirect evidence for the involvement of such species in the catalytic reaction. Although complexes such as $[Fe_3(CO)_{10}(NR)]$ (1) (R = ethyl) and $[Fe_3(CO)_9(NR)_2]$ (2) (R = ethyl or isopropyl) have been isolated from the reaction of nitroalkanes with $[Fe_3(CO)_{12}]$, unequivocal *X*-ray structural data are not available.[3] In this paper we report the isolation of analogous products from the reaction of nitrobenzene and $[Ru_3(CO)_{12}]$, and the *X*-ray structural analysis of $[Rh_3(CO)_{10}(NPh)]$ (3).

Results and Discussion

Reaction of $[Ru_3(CO)_{12}]$ with $PhNO_2$ at elevated temperatures (⩾ 100 °C) leads to the formation of complex (3) and $[Ru_3(CO)_9(NPh)_2]$ (4) in low (⩽ 5%) yields. In contrast to the reaction of $[Fe_3(CO)_{12}]$ with nitroalkanes, $[Ru_3(CO)_{12}]$ does not react with $PhNO_2$ at ambient temperatures, nor could species like (3) or (4) be isolated from $[Fe_3(CO)_{12}]$ and nitrobenzene.

Yields of (3) and (4) are somewhat improved (< 15%) by carrying out the reaction under an atmosphere of CO. However, under high pressure ($\geqslant 7 \times 10^6$ Pa) of CO only unreacted $[Ru_3(CO)_{12}]$ and no (3) or (4) could be obtained. Thermal disproportionation of (3) under an inert atmosphere and in solution leads to the formation of complex (4) and other as yet uncharacterised products. In the reaction between $PhNO_2$ and $[Ru_3(CO)_{12}]$ carried out in n-octane, an i.r. band at 2 340 cm^{-1} indicated CO_2 formation. The overall reaction may therefore proceed as in equations (i) and (ii).

$$[Ru_3(CO)_{12}] + PhNO_2 \longrightarrow [Ru_3(CO)_{10}(NPh)] + 2CO_2 \quad \text{(i)}$$

$$2[Ru_3(CO)_{10}(NPh)] \longrightarrow [Ru_3(CO)_9(NPh)_2] + \text{other products} \quad \text{(ii)}$$

Both complexes (3) and (4) have been characterised fully on the basis of their microanalytical, ^1H n.m.r., i.r., and mass-spectrometric data. The solution i.r. spectrum of (3) suggests a symmetrical structure with a triply bridging NPh and carbonyl groups. The more complicated pattern of terminal CO absorptions in the solution i.r. spectrum of (4) indicates lower symmetry.

The crystal structure determination (Figure, Tables 1 and 2) confirms local C_{3v} symmetry for the molecular skeleton, and the presence of triply bridging NPh and CO groups on opposite sides of the Ru_3 triangle. There are two independent molecules in the asymmetric unit, with slightly different phenyl-group orientations, but otherwise very similar dimensions. The average Ru–Ru bond of 2.746(5) Å [estimated standard deviation (e.s.d.) calculated from the scatter of the six independent values] is shorter than the value of 2.854(4) Å in $[Ru_3(CO)_{12}]$, which may be caused by steric repulsion between the axial carbonyl groups in the latter. Similarly, the mean Fe–Fe distance in $[Fe_3(CO)_{10}(NSiMe_3)]$, which also possesses triply bridging CO and NR ligands, is 2.535(2) Å whilst those in $[Fe_3(CO)_{12}]$ are 2.680(2) and 2.558(1) Å for the unbridged and bridged Fe–Fe bonds respectively.[4,5] The average Ru–C and Ru–N bond distances for the triply bridging CO and NPh groups in (3) are 2.172(8) and 2.055(5) Å respectively. To our knowledge this is the first *X*-ray structural characterisation of a ruthenium cluster with a triply bridging CO group.

The observed local C_{3v} symmetry in complex (3) and the lack of it in (4) as evident from solution i.r. data could be rationalised by referring to the frontier orbitals of the Fe_3-

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† μ_3-Carbonyl-μ_3-phenylimido-tris(tricarbonylruthenium).

Supplementary data available (No. SUP 23669, 35 pp.): thermal parameters, H-atom co-ordinates, full list of bond lengths and angles, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Atomic parameters (× 10^4) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	3 708(1)	1 394(1)	1 458(1)	Ru(1′)	7 454(1)	6 755(1)	1 668(1)
Ru(2)	1 521(1)	1 680(1)	1 417(1)	Ru(2′)	8 529(1)	6 354(1)	878(1)
Ru(3)	2 421(1)	−87(1)	1 934(1)	Ru(3′)	6 333(1)	6 430(1)	843(1)
C(11)	4 613(5)	2 536(5)	1 781(2)	C(11′)	7 479(6)	8 261(6)	1 962(2)
O(11)	5 113(4)	3 208(4)	1 973(2)	O(11′)	7 503(5)	9 145(4)	2 136(2)
C(12)	4 019(6)	2 131(7)	882(2)	C(12′)	8 627(5)	6 286(5)	2 082(2)
O(12)	4 208(5)	2 542(6)	552(2)	O(12′)	9 295(4)	6 035(5)	2 330(2)
C(13)	4 829(5)	259(5)	1 456(2)	C(13′)	6 304(5)	6 220(6)	2 028(2)
O(13)	5 474(4)	−433(5)	1 448(2)	O(13′)	5 624(4)	5 872(5)	2 242(2)
C(21)	799(5)	2 851(6)	1 760(3)	C(21′)	9 233(5)	7 591(6)	548(2)
O(21)	394(4)	3 530(5)	1 979(2)	O(21′)	9 587(4)	8 308(5)	346(2)
C(22)	222(7)	862(7)	1 238(3)	C(22′)	8 704(5)	5 273(6)	387(2)
O(22)	−513(5)	343(7)	1 125(3)	O(22′)	8 852(4)	4 613(5)	103(2)
C(23)	1 564(7)	2 678(7)	890(3)	C(23′)	9 852(6)	5 953(6)	1 196(3)
O(23)	1 562(7)	3 293(6)	586(2)	O(23′)	10 656(4)	5 741(6)	1 363(2)
C(31)	2 366(5)	−11(5)	2 597(2)	C(31′)	5 550(5)	7 718(7)	567(2)
O(31)	2 332(4)	68(4)	2 977(2)	O(31′)	5 121(5)	8 514(5)	412(2)
C(32)	3 442(6)	−1 363(6)	1 973(2)	C(32′)	5 033(5)	5 795(6)	1 091(2)
O(32)	4 034(4)	−2 106(5)	1 983(2)	O(32′)	4 279(4)	5 395(6)	1 220(2)
C(33)	1 139(6)	−1 017(6)	1 916(2)	C(33′)	6 266(5)	5 618(6)	271(2)
O(33)	386(5)	−1 562(6)	1 908(2)	O(33′)	6 248(4)	5 129(5)	−70(2)
C(4)	2 651(5)	1 761(5)	2 012(2)	C(4′)	7 457(5)	7 797(5)	1 051(2)
O(4)	2 730(3)	2 397(3)	2 325(1)	O(4′)	7 473(3)	8 808(3)	976(1)
N(5)	2 479(3)	296(4)	1 249(1)	N(5′)	7 402(3)	5 389(4)	1 211(1)
C(51)	2 405(4)	−454(5)	858(2)	C(51′)	7 379(4)	4 158(5)	1 286(2)
C(52)	2 319(6)	6(6)	424(2)	C(52′)	7 884(6)	3 675(5)	1 670(3)
C(53)	2 260(6)	−719(7)	43(2)	C(53′)	7 874(6)	2 465(6)	1 732(3)
C(54)	2 243(6)	−1 909(7)	95(2)	C(54′)	7 394(5)	1 743(5)	1 431(3)
C(55)	2 314(7)	−2 363(6)	526(2)	C(55′)	6 889(6)	2 201(5)	1 062(2)
C(56)	2 373(6)	−1 665(6)	900(2)	C(56′)	6 861(6)	3 404(5)	986(2)

Table 2. Selected distances (Å) and angles (°) with estimated standard deviations in parentheses

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
Ru(1)–Ru(2)	2.741(1)	2.754(1)	Ru(3)–C(33)	1.917(7)	1.912(7)
Ru(1)–Ru(3)	2.750(1)	2.760(1)	Ru(1)–C(4)	2.171(6)	2.160(6)
Ru(2)–Ru(3)	2.735(1)	2.734(1)	Ru(2)–C(4)	2.195(6)	2.195(6)
Ru(1)–C(11)	1.943(6)	1.924(7)	Ru(3)–C(4)	2.143(6)	2.167(6)
Ru(1)–C(12)	1.937(7)	1.933(6)	Ru(1)–N(5)	2.053(4)	2.054(4)
Ru(1)–C(13)	1.907(6)	1.914(7)	Ru(2)–N(5)	2.053(4)	2.060(4)
Ru(2)–C(21)	1.919(7)	1.942(7)	Ru(3)–N(5)	2.055(4)	2.055(4)
Ru(2)–C(22)	1.923(8)	1.914(7)	C(4)–O(4)	1.167(7)	1.177(7)
Ru(2)–C(23)	1.919(9)	1.914(7)	N(5)–C(51)	1.428(7)	1.425(7)
Ru(3)–C(31)	1.944(7)	1.924(7)	C(4) · · · N(5)	2.790(10)	2.793(10)
Ru(3)–C(32)	1.935(7)	1.943(7)			

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
Ru(2)–Ru(1)–Ru(3)	59.8(1)	59.4(1)	Ru(1)–Ru(3)–N(5)	48.0(1)	47.8(1)
Ru(2)–Ru(1)–C(4)	51.5(2)	51.3(2)	Ru(2)–Ru(3)–N(5)	48.2(1)	48.4(1)
Ru(3)–Ru(1)–C(4)	50.0(2)	50.5(2)	C(4)–Ru(3)–N(5)	83.3(2)	82.7(2)
Ru(2)–Ru(1)–N(5)	48.1(1)	48.1(1)	Ru(1)–C(4)–Ru(2)	77.8(2)	78.5(2)
Ru(3)–Ru(1)–N(5)	48.0(1)	47.8(1)	Ru(1)–C(4)–Ru(3)	79.2(2)	79.3(2)
C(4)–Ru(1)–N(5)	82.7(2)	83.0(2)	Ru(2)–C(4)–Ru(3)	78.2(2)	77.6(2)
Ru(1)–Ru(2)–Ru(3)	60.3(1)	60.4(1)	Ru(1)–C(4)–O(4)	132.1(5)	134.4(5)
Ru(1)–Ru(2)–C(4)	50.7(2)	50.2(2)	Ru(2)–C(4)–O(4)	132.6(4)	132.8(5)
Ru(3)–Ru(2)–C(4)	50.1(2)	50.7(2)	Ru(3)–C(4)–O(4)	134.7(5)	132.1(4)
Ru(1)–Ru(2)–N(5)	48.1(1)	47.9(1)	Ru(1)–N(5)–Ru(2)	83.7(2)	84.1(2)
Ru(3)–Ru(2)–N(5)	48.3(1)	48.3(1)	Ru(1)–N(5)–Ru(3)	84.0(2)	84.4(2)
C(4)–Ru(2)–N(5)	82.1(2)	82.0(2)	Ru(2)–N(5)–Ru(3)	83.5(2)	83.3(2)
Ru(1)–Ru(3)–Ru(2)	60.0(1)	60.2(1)	Ru(1)–N(5)–C(51)	128.9(4)	130.5(3)
Ru(1)–Ru(3)–C(4)	50.8(2)	50.3(2)	Ru(2)–N(5)–C(51)	129.4(3)	128.3(3)
Ru(2)–Ru(3)–C(4)	51.8(2)	51.6(2)	Ru(3)–N(5)–C(51)	130.4(4)	129.5(3)

$(CO)_9$ unit as constructed by Schilling and Hoffmann.[6] There are three low-lying cyclopropenium-type acceptor orbitals of *a′* and *e′* symmetry which could accommodate a maximum of six electrons and are ideally set up to interact with capping ligands. Ground-state structures of molecules such as $[Ru_3H_2(CO)_9(C_2H_2)]$ or $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PR_3)]$ with acetylene and ' $Pt(CO)(PR_3)$ ' as the capping groups can be rationalised in this way. The six-electron requirement of

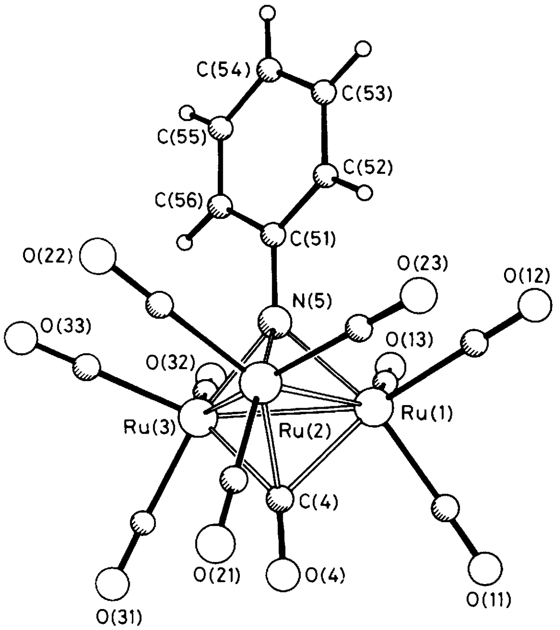

Figure. One molecule of $[Ru_3(CO)_{10}(NPh)]$ (3) showing the atom-numbering scheme. The hydrogen atoms are numbered according to the carbons to which they are attached, and the carbonyl carbons have the same numbers as the corresponding oxygen atoms. Corresponding atoms in the second molecule are denoted by primes

the low-lying acceptor levels of the ' $Ru_3(CO)_9$ ' unit could therefore be satisfactorily met in (3) by considering the triply bridging CO and NPh groups as two- and four-electron donors respectively. However, this is not the case with complex (4) where a total of eight electrons, four from each NPh group, will have to be accommodated. Presumably, removal of local C_{3v} symmetry in (4) produces another low-lying acceptor level which accommodates the extra electron pair.

Experimental

Infrared spectra were taken on a Perkin-Elmer 377 grating spectrometer. A Carlo-Erba 1106 instrument was used for microanalyses.

Syntheses of Complexes (3) *and* (4).†—The complex $[Ru_3(CO)_{12}]$ (0.64 g, 1 mmol) was heated with $PhNO_2$ (0.18 g, 1.5 mol) in n-octane (30 cm^3) at 110 °C while a gentle stream of CO was bubbled through the solution. After 6 h of reaction the solvent was removed under reduced pressure and the residue subjected to thin-layer chromatography with n-hexane as eluant. After repeated chromatography an orange band, the only one that moved, separated into a red band (4) followed by a yellow one (3). Both the complexes were recrystallised from n-hexane at 0 °C, the respective yields of (3) and (4) being 0.1 (15) and 0.09 g (12%) (Found: C, 28.6; H, 0.6; N, 2.1. Calc. for $C_{16}H_5NO_{10}Ru_3$: C, 28.5; H, 0.7; N, 2.1%. Found: C, 34.3; H, 1.6; N, 3.7. Calc. for $C_{21}H_{10}N_2O_9Ru_3$: C, 34.2; H, 1.4; N, 3.8%). Infrared spectra (cyclohexane): (3), 2 110w, 2 075vs, 2 030s, 2 015w, and 1 740br, m cm^{-1}; (4), 2 092vw, 2 072vs, 2 048vs, 2 022, 2 015, 2 012m, 1 975m, and 1 950w cm^{-1}. Mass spectra: (3), molecular ion peak at 674, with successive loss of ten CO groups which overlaps with the fragmentation pattern derived from loss of PhN; (4), molecular ion peak at 737, with successive loss of nine CO groups. Proton n.m.r. spectrum for both (3) and (4): multiplets at 7.3 and 7.05 p.p.m. respectively in $(CD_3)_2CO$.

Crystal Data.—$C_{16}H_5NO_{10}Ru_3$, $M = 674.43$, Monoclinic, space group $P2_1/n$, $a = 12.457(1)$, $b = 11.428(1)$, $c = 29.234(2)$ Å, $\beta = 92.38(1)°$, $U = 4\,158.1$ Å^3, $Z = 8$, $D_c = 2.154$ g cm^{-3}, $F(000) = 2\,560$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 21.6$ cm^{-1}, crystal dimensions 0.2 × 0.54 × 0.2 mm.

Data were collected by a profile-fitting procedure[7] on a Stoe four-circle diffractometer in the range $7 < 2\theta < 45°$, affording 5 420 unique reflections. After Lorentz, polarisation, and semi-empirical absorption corrections, the 4 817 data with $F > 4\sigma(F)$ were employed for all calculations, which were performed using the SHELXTL program system (written by G. M. S.). The structure was solved by direct methods (to locate Ru) and successive difference syntheses, and refined to $R' = \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o| = 0.040$, and $R = \Sigma\Delta/\Sigma|F_o| = 0.036$ with all non-hydrogen atoms anisotropic, a riding model for the hydrogen atoms [H on the C–C–C external bisector, $U(H) = 1.2\ U_{eq}(C)$, and C–H 0.96 Å], and weights $w^{-1} = [\sigma^2(F) + 0.000\,25\ F^2]$. An extinction parameter x refined to $5.7(3) \times 10^{-4}$, where $F_c{}^* = F_c/(1 + 0.002\,x\,F_c{}^2/\sin 2\theta)^{\frac{1}{4}}$. Final co-ordinates are given in Table 1, bond lengths and angles in Table 2.

Acknowledgements

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References

1 A. F. M. Iqbal, *Chem. Tech.* (*Leipzig*), 1974, 566; J. F. Knitton, ' Catalysis in Organic Synthesis,' Academic Press, New York, 1976.
2 H. Alper and K. E. Hashan, *J. Am. Chem. Soc.*, 1981, **103**, 6514; H. Alper and H. des Abbayes, *ibid.*, 1977, **99**, 98; H. Alper and S. Amaratunga, *Tetrahedron Lett.*, 1980, **21**, 2603; R. C. Ryan, G. M. Wilemon, M. P. Dalsanto, and C. U. Pittman, *J. Mol. Catal.*, 1979, **5**, 319.
3 S. Aime, G. Garuasio, L. Milone, R. Rossetti, and P. L. Stanghellini, *J. Chem. Soc., Dalton Trans.*, 1978, 534.
4 B. L. Barnett and C. Krüger, *Angew. Chem.*, 1971, **83**, 969.
5 F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, 1974, **96**, 4155.
6 B. E. R. Schilling and R. Hoffmann, *J. Am. Chem. Soc.*, 1979, **100**, 3456.
7 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.

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† *Note added at proof:* it has recently come to our notice that a similar preparation of (3) and (4) (without *X*-ray analysis) was reported by E. Sappa and L. Milone, *J. Organomet. Chem.*, 1973, **61**, 383.