Reaction of Nitrobenzene with $[M_3(CO)_{12}]$ (M = Fe or Ru) in the Presence of $[Co_2(CO)_8]$: Isolation and Structure of $[Ru_3(CO)_7(NPh)(\eta^6\text{-}C_6H_6)]$ †

Amitabha Basu, Sumit Bhaduri,* and Hanif Khwaja
Alchemie Research Centre, CAFI Site, P.O. Box 155, Thane-Belapur Road, Thane 400 601, Maharashtra, India
Peter G. Jones,* Karen Meyer-Bäse, and George M. Sheldrick
Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, D-3400 Göttingen, Federal Republic of Germany

The complexes $[Ru_3(CO)_7(NPh)(C_6H_6)]$ (**1**) and $[FeCo_2(CO)_9(NPh)]$ (**2**) are formed in the reactions between $PhNO_2$ and $[M_3(CO)_{12}]$ (M = Ru or Fe) only when $[Co_2(CO)_8]$ is present. The structure of (**1**) has been determined by *X*-ray diffraction; it contains triply bridging CO and PhN ligands and an η^6-benzene ligand co-ordinated to only one metal atom.

Synthesis of phenyl isocyanate or phenylcarbamate derivatives by the direct carbonylation of nitrobenzene is of industrial importance.[1] Recently a few reports have appeared on this and other related reactions where carbonyl clusters, particularly $[Ru_3(CO)_{12}]$, have been used as efficient catalysts.[2] Here we report that the addition of $[Co_2(CO)_8]$ to reaction systems consisting of $[M_3(CO)_{12}]$ (M = Fe or Ru) and $PhNO_2$ has a remarkable effect on the nature of metal complexes formed in the reactions. A single-crystal *X*-ray structure determination of $[Ru_3(CO)_7(NPh)(C_6H_6)]$ (**1**), a complex formed only through the mediation of $[Co_2(CO)_8]$, is reported.

Results and Discussion

Although $[Ru_3(CO)_{12}]$ is an active precatalyst in the conversion of nitrobenzene to phenyl isocyanate by CO, $[Fe_3(CO)_{12}]$ under the same conditions (*e.g.* 160 °C, 300 lb in^{-2}, C_6H_6 solvent, 5 h) shows little activity.[3] Addition of $[Co_2(CO)_8]$ to both the reaction systems results in the formation of azobenzene as one of the major products. Reactions of $[M_3(CO)_{12}]$ (M = Fe or Ru) with $PhNO_2$ under milder conditions, with or without the addition of $[Co_2(CO)_8]$, are described in the Scheme.

In the absence of $[Co_2(CO)_8]$, reaction of $PhNO_2$ and $[Fe_3(CO)_{12}]$ leads to the precipitation of insoluble iron oxides. However, under the same reaction conditions, addition of $[Co_2(CO)_8]$ yields complexes (**2**) and (**5**). Characterisation of (**2**) is based on microanalytical data, and mass, n.m.r., and solution i.r. spectra. The crystal structure determination of (**5**) was reported recently.[4]

Addition of $[Co_2(CO)_8]$ to the $[Ru_3(CO)_{12}]/PhNO_2$ reaction system gives (**1**) and (**4**) but not (**3**). Small quantities of $[Co_4(CO)_9(C_6H_6)]$ are also isolated from the reaction system; reaction of this complex with (**3**) produces (**1**), also in small quantities. Crystal structure determinations of (**3**) and (**4**) have recently been reported.[5]

The structure of (**1**) is shown in the Figure; it is consistent with its analytical and spectroscopic data. The ruthenium atoms form an approximately equilateral triangle with Ru–Ru (av.) 2.708 Å. The triangle is triply bridged on one side by the PhN ligand and on the other side, very asymmetrically, by CO [C–Ru(2) 1.981, C–Ru(1) 2.336, C–Ru(3) 2.354 Å). Ru(1) and Ru(3) both bear three terminal CO ligands and Ru(2) an η^6-benzene ligand. Arene ligands are not a common feature in metal cluster chemistry; one recent example is the carbide $[Ru_6C(CO)_{11}(C_6H_6)_2]$.[6]

Experimental

Infrared and n.m.r. spectra were recorded on a Perkin-Elmer 377 grating spectrometer and a Bruker 80 MHz instrument respectively. A Carlo Erba 1106 instrument was used for C, H, and N microanalyses; iron and cobalt analyses were performed by atomic absorption spectrophotometry using an Instrumentation Laboratory TL 751 instrument.

Synthesis of (**1**) *and* (**2**).—A solution of $[Ru_3(CO)_{12}]$ (0.214 g, 0.33 mmol), nitrobenzene (0.2 g, 1.5 mmol), and $[Co_2(CO)_8]$ (0.342 g, 1 mmol) in benzene (100 cm^3) was stirred and refluxed under CO for 5 h. The resultant solution was taken to dryness, extracted with dichloromethane, and subjected to thin-layer chromatography (t.l.c.) with n-hexane as eluant. $[Ru_3(CO)_9(NPh)_2]$, $[Co_4(CO)_9(C_6H_6)]$, and unreacted $[Ru_3(CO)_{12}]$ moved on the plate while (**1**) remained near the baseline. It was extracted with dichloromethane and subjected to t.l.c. again with 40% dichloromethane in hexane as eluant. The complex was crystallized from dichloromethane and n-hexane (Found: C, 34.3; H, 1.8; N, 2.0. Calc. for $C_{19}H_{11}NO_7Ru_3$: C, 34.1; H, 1.6; N, 2.1%).

Compound (**2**) was synthesized under the same conditions using $[Fe_3(CO)_{12}]$ (2.02 g, 4 mmol), nitrobenzene (2.4 g, 19.5 mmol), and $[Co_2(CO)_8]$ (4.1 g, 12 mmol) in benzene (200 cm^3). The eluant for t.l.c. was 1% dichloromethane in hexane; (**2**) moves to the top of the plate as a dark brown band (Found: C, 34.5; H, 1.1; Co, 22.8; Fe, 10.8; N, 2.5. Calc. for $C_{15}H_5Co_2FeNO_9$: C, 34.8; H, 1.0; Co, 22.8; Fe, 10.8; N, 2.7%).

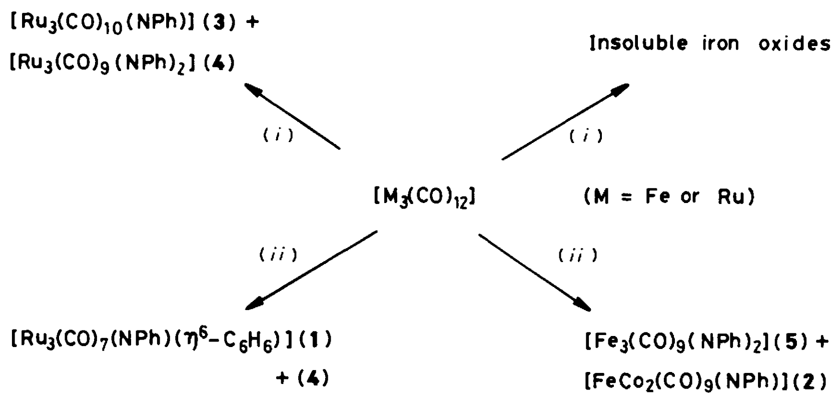
Spectral Data for (**1**) *and* (**2**).—Infrared spectra (n-hexane):

---

† 3-(1—6-η-Benzene)-μ_3-carbonyl-1,1,1,2,2,2-hexacarbonyl-μ_3-(phenylimido)-*triangulo*-triruthenium.

Supplementary data available: complete bond lengths and angles, H-atom co-ordinates, structure factors, and thermal parameters may be obtained from the Fachinformationszentrum Energie Physik Mathematik, 7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany, quoting reference no. CSD 51801 and the full literature citation.

Non-S.I. unit employed: lb in^{-2} ≈ 6895 Pa.



Scheme. (*i*) C_6H_6, 80 °C, 5 h, $[M_3(CO)_{12}]:PhNO_2 = 1:1.5$; (*ii*) C_6H_6, 80 °C, 5 h, $[M_3(CO)_{12}]:PhNO_2:[Co_2(CO)_8] = 1:1.5:1$

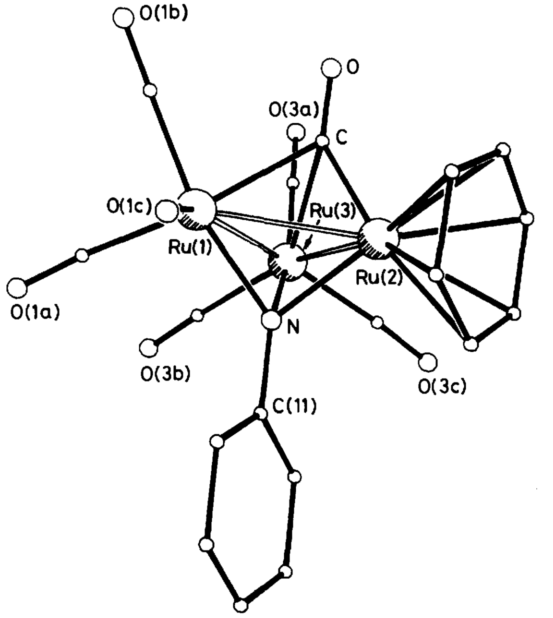


Figure. The molecule of (**1**) in the crystal (H atoms omitted, radii arbitrary). Selected bond lengths (Å): Ru(1)–Ru(2) 2.695(2), Ru(1)–Ru(3) 2.726(2), Ru(2)–Ru(3) 2.704(2), N–Ru(1) 2.016(9), N–Ru(2) 2.029(9), N–Ru(3) 2.043(9), C–Ru(1) 2.336(11), C–Ru(2) 1.981(12), C–Ru(3) 2.354(11), Ru(2)–C(benzene) 2.193—2.240(13) Å

(**1**), 2 074s, 2 046vs, 2 010vs, 1 986s, 1 976m, and 1 745m, br cm^{-1}; (**2**), 2 096m, 2 058vs, 2 042vs, 2 034s (sh), 2 026w (sh), 1 975m, and 1 965m cm^{-1}. Proton n.m.r. spectra for both (**1**) and (**2**): multiplets around 7.1 p.p.m. in $CDCl_3$.

X-Ray Structure Determination of(**1**).—*Crystal data.* $C_{19}H_{11}NO_7Ru_3$, $M = 668.5$, monoclinic, space group $P2_1/n$, $a = 8.618(2)$, $b = 15.455(2)$, $c = 16.446(3)$ Å, $\beta = 91.92(2)°$, $U = 2\,189.3$ Å^3 (refined from 2θ values of 40 strong reflections in the range 20—23°), graphite-monochromated Mo-K_α radiation ($\lambda = 0.710\,69$ Å), $Z = 4$, $D_c = 2.03$ g cm^{-3}, $F(000) = 1\,280$. Reddish brown tablets: crystal dimensions 0.15 × 0.1 × 0.05 mm, $\mu = 2.0$ mm^{-1}.

Data collection and processing. Stoe-Siemens four-circle diffractometer, 4 233 profile-fitted intensities[7] ($2\theta_{max.}$ 50°), 3 843 unique, 2 428 with $F > 4\sigma(F)$ used for all calculations (program system SHELXTL[8]). Absorption correction based on ψ-scans (transmissions 0.77—0.89). No crystal decay.

Structure solution and refinement. Ruthenium atoms from Patterson function, other non-H atoms from difference syntheses. Least-squares refinement on F to R 0.061, R' 0.048 [non-H atoms anisotropic, H atoms included using a riding model with C–H 0.96 Å, U(H) = 1.2 U_{eq}(C); weighting scheme $w^{-1} = \sigma^2(F) + 0.0003\,F^2$; 271 parameters]. Final atomic co-ordinates are given in the Table.

Acknowledgements

We thank the Fonds der Chemischen Industrie for financial support.

Table. Atomic co-ordinates (× 10^4) for (**1**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	292(1)	1 896(1)	2 563.9(0.5)	C(3a)	−1 380(15)	2 522(8)	4 656(7)
Ru(2)	2 209(1)	1 242(1)	3 737.8(0.5)	C(3b)	−79(14)	3 793(8)	3 712(7)
Ru(3)	472(1)	2 649(1)	4 062.8(0.5)	C(3c)	1 741(16)	2 904(8)	4 993(7)
N	2 086(9)	2 426(5)	3 205(4)	C(11)	3 394(12)	2 921(6)	2 959(6)
O	−1 092(9)	759(5)	3 985(4)	C(12)	4 093(15)	3 513(8)	3 468(7)
C	−81(12)	1 183(7)	3 795(6)	C(13)	5 370(15)	3 999(8)	3 233(9)
O(1a)	−641(10)	3 501(5)	1 600(5)	C(14)	5 959(15)	3 895(8)	2 474(8)
O(1b)	−2 816(10)	1 041(6)	2 203(5)	C(15)	5 267(16)	3 310(8)	1 981(9)
O(1c)	1 890(12)	891(6)	1 234(6)	C(16)	3 988(14)	2 810(8)	2 208(7)
O(3a)	−2 487(11)	2 436(7)	5 015(6)	C(21)	4 806(13)	1 069(7)	3 796(7)
O(3b)	−348(12)	4 481(6)	3 544(6)	C(22)	4 155(12)	488(7)	3 225(7)
O(3c)	2 523(12)	3 092(7)	5 542(5)	C(23)	2 975(14)	−81(7)	3 467(8)
C(1a)	−346(13)	2 902(7)	1 957(7)	C(24)	2 496(14)	−80(7)	4 267(8)
C(1b)	−1 666(13)	1 349(7)	2 319(6)	C(25)	3 081(14)	522(8)	4 807(7)
C(1c)	1 301(14)	1 269(8)	1 708(6)	C(26)	4 262(14)	1 083(8)	4 596(7)

References

1 G. W. Parshall, 'Homogeneous Catalysis,' Wiley, New York, 1980, p. 93 and refs. therein; Mitsubishi Chem. Ind. Co., Jap. P. 81 118 054/1981.

2 S. Ceuini, M. Pizzoth, C. Crotti, F. Porta, and G. LaMonica, *J. Chem. Soc., Chem. Commun.*, 1984, 1286; H. Alper and K. E. Hashem, *J. Am. Chem. Soc.*, 1981, **103**, 6514; H. Alper and L. C. Damude, *Organometallics*, 1982, **1**, 579; S. Bhaduri, K. S. Gopalkrishnan, W. Clegg, P. G. Jones, G. M. Sheldrick, and D. Stalke, *J. Chem. Soc., Dalton Trans.*, 1984, 1765.

3 S. Bhaduri, K. R. Sharma, and K. Gopalkrishnan, U.S.P. 4 491 670/1983.

4 W. Clegg, G. M. Sheldrick, D. Stalke, S. Bhaduri, and H. K. Khwaja, *Acta Crystallogr., Sect. C*, 1984, **40**, 2045.

5 S. Bhaduri, K. S. Gopalkrishnan, G. M. Sheldrick, W. Clegg, and D. Stalke, *J. Chem. Soc., Dalton Trans.*, 1983, 2339; W. Clegg, G. M. Sheldrick, D. Stalke, S. Bhaduri, and K. S. Gopalkrishnan, *Acta Crystallogr., Sect. C*, 1984, **40**, 927.

6 M. P. Gomez-Sal, B. F. G. Johnson, J. Lewis, P. R. Raithby, and A. H. Wright, *J. Chem. Soc., Chem. Commun.*, 1985, 1682 and refs. therein.

7 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.

8 SHELXTL, G. M. Sheldrick, University of Göttingen, 1978.

Received 22nd January 1986; *Paper* 6/159