Pergamon

PII: S0277–5387(96)00574–8

Polyhedron Vol. 16, No. 14, pp. 2429–2433, 1997

0277–5387/97 $17.00+0.00

Ruthenium-mediated dehydration of benzaldehyde oxime. X-ray crystal structure of the mixed-valence compound $[RuBr(N{\equiv}CPh)_5][RuBr_4(N{\equiv}CPh)_2]\cdot PhCH_2OH$

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(Received 23 October 1996; accepted 15 November 1996)

Abstract—The reaction between $RuBr_3\cdot xH_2O$ and benzaldehyde oxime in aqueous 6 M HBr results in facile metal-assisted dehydration of the oxime and concomitant partial reduction of ruthenium(III) to produce the mixed-valence ruthenium(III)–ruthenium(II) compound $[RuBr(N{\equiv}CPh)_5][RuBr_4(N{\equiv}CPh)_2]$. This ionic complex has been structurally characterized as the monobenzyl alcohol solvate, $[RuBr(N{\equiv}CPh)_5][RuBr_4(N{\equiv}CPh)_2]\cdot PhCH_2OH$. © 1997 Elsevier Science Ltd

Keywords: oximes; nitriles; dehydration; ligand reactivity; mixed-valence complexes; Ru complexes.

Although the synthetic and structural chemistry of metal-oxime complexes has been extensively studied [1], metal-mediated reactions of oxime ligands have received little attention. Some recently reviewed data [1] show that the reactivity of coordinated aldoxime and ketoxime species and their complexes is rich and far from being fully explored.

In organic chemistry, it is well-documented that aldoximes, $RC(H){=}NOH$, are useful starting materials for the synthesis of nitriles *via* dehydration, but these reactions usually require harsh conditions and/or very reactive dehydrating agents. Thus, the dehydration of benzaldehyde oxime can be achieved by use of sulfuryl chloride fluoride [2], $SO_2\cdot NMe_3$ [3], dichlorocarbene [4] or dipyridyl carbonate [5]. As far as the metal-mediated dehydration of oximes is concerned, work in this area is quite scarce, although several reports [6–8] describing the dehydration of oximes and the formation of metal-bound nitriles have been published. These examples include concerted deaquation and dealkylation of ketoximes, $MeRC{=}NOH$, by the ruthenium(II) complex $[Ru(NH_3)_5(H_2O)]^{2+}$ to produce $[Ru(NH_3)_5(N{\equiv}CMe)]^{2+}$ [6], conversion of the aldoximes during the reaction between $[(\eta^6\text{-}C_6H_6)OsHI(PMeBu^t_2)]$ and $AgPF_6$ in the presence of $HON{=}CHR$ (R = Me, Ph) to give $[(\eta^6\text{-}C_6H_6)OsH(N{\equiv}CR)(PMeBu^t_2)]$ [7], and dehydration of $HON{=}CHR$ (R = Me, Ph, *p*-C_6H_4OMe) on treatment with $[W(CO)_5(THF)]$ [8]. In addition, some workers have studied the solid-state thermal elimination of water from oxime-containing complexes, but no convincing evidence for the formation of nitriles was given [9,10].

During investigation of the reactivity of both oxime [1,11] and nitrile ligands [12], we became interested in the dehydration of aldoximes resulting in the generation of nitrile complexes. As starting materials for this study, we employed $RuBr_3\cdot xH_2O$ and benzaldehyde oxime, $PhC(H){=}NOH$. It was expected that the high nitrilophilicity of the ruthenium ion would drive the dehydration reaction. Here we report that the reaction between ruthenium(III) bromide and benzaldehyde oxime in aqueous 6 M HBr produces the mixed-valence ruthenium(III)–ruthenium(II)

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compound $[RuBr(N{\equiv}CPh)_5][RuBr_4(N{\equiv}CPh)_2]$. The latter ionic complex has been structurally characterized as the mono benzyl alcohol solvate and these results are included herein.

EXPERIMENTAL

Materials and instrumentation

$RuBr_3{\cdot}xH_2O$ (Reakhim) and *syn*-benzaldehyde oxime (Lancaster) were obtained from commercial sources and were used as received. $RuBr_3{\cdot}xH_2O$ was analyzed for Ru before use and data obtained were recalculated to account for anhydrous $RuBr_3$ in order to calculate stoichiometry and reaction yields. C, H and N elemental analyses were carried out by the Microanalytical Service, Osaka City University. Ru elemental analysis was performed by the authors. FAB mass spectra were obtained with a JEOL JMS-AX500 mass-spectrometer, while GC-MS analysis was carried out on a LKB-2091 instrument. For TLC, Riedel–deHaën 60F254 SiO_2 plates with a layer thickness of 0.2 mm were used. Decomposition points were determined for samples in capillary tubes. IR spectra were recorded on a Perkin–Elmer 1650 FT-IR instrument, using Nujol mulls between CsI windows.

Synthetic work and characterization

Benzaldehyde oxime (1.2 cm^3L, 9.9 mmol) was added to a solution of $RuBr_3$ (0.20 g, 0.59 mmol) in aqueous 6 M HBr (2 cm^3L) and the mixture was heated at 60°C for 10 min and then cooled to room temperature. Water (5 cm^3L) was added to the reaction which was extracted with two 3 cm^3L portions of $CHCl_3$. The chloroform solution was evaporated to 1 cm^3L and ethanol (0.1 cm^3) was added followed by diethyl ether (40 cm^3L). A precipitate gradually formed over the course of 2–3 h, which was collected on a filter, washed with three 5 cm^3L portions of water, dried in air on a filter and then washed with three 5 cm^3L portions of Et_2O and dried in a vacuum desiccator over NaOH. The yield of $[RuBr(N{\equiv}CPh)_5][RuBr_4(N{\equiv}CPh)_2]$ was 0.09 g, 23% (based on Ru). Found: C, 43.7; H, 2.7; N, 7.4; Ru, 15.4. Calc. for $C_{49}H_{35}Br_5N_7Ru_2$: C, 44.5; H, 2.7; N, 7.4; Ru, 15.3%. FAB^+-MS, *m/z*: 697 ($[M-H]^+$). FAB^--MS, *m/z*: 627 ($[M-H]^+$). The compound had no characteristic melting point. On heating in a capillary it decomposed from *ca* 160°C. TLC on SiO_2, $CHCl_3$: $Me_2CO = 10:1$, $R_f = 0.45$. Visible electronic absorption spectrum in $CHCl_3$, λ_{max} ($\log \varepsilon$): 511 (3.52), 571 (3.53), and 668 (2.60) nm. IR spectrum, cm^{-1}: 2358 w and 2275 w, ν(CN).

Recrystallization of $[RuBr(N{\equiv}CPh)_5][RuBr_4(N{\equiv}CPh)_2]$ from benzyl alcohol gave crystals of the monosolvate, $[RuBr(N{\equiv}CPh)_5][RuBr_4(N{\equiv}CPh)_2]{\cdot}PhCH_2OH$, suitable for X-ray analysis. Found: C, 46.6; H, 3.1; N, 6.8. Calc. for $C_{56}H_{43}Br_5N_7ORu_2$: C, 47.0; H, 3.0; N, 6.8%. FAB^+-MS, *m/z*: 697 ($[M-H]^+$). FAB^--MS, *m/z*: 627 ($[M-H]^+$). The solvate had no characteristic melting point. On heating in a capillary it decomposed from *ca* 145°C. IR spectrum, cm^{-1}: 2379 vw, 2333 vw and 2251 w, ν(CN).

X-ray crystallography

Diffraction data were collected on an Enraf–Nonius CAD-4 diffractometer. Cell parameters were obtained from 20 centered reflections with $10.0 < \theta < 15.0°$, 3772 collected reflections, of which 3760 [$R_{int} = 0.0086$] were unique, observed with $I \geqslant 3\sigma(I)$ were measured up to 45° by the $\theta/2\ \theta$ scan technique. Range of *hkl*: $h = 0$ to 12, $k = -12$ to 14, $l = -21$ to 21. Diffractometer data were processed by the program PROFIT [13] with profile analysis of reflections. The structure was solved by means of Fourier synthesis based upon the Ru-atom coordinates obtained from a Patterson synthesis using the SHELXTL package [14]. After that, all reflections with $I < 3\sigma(I)$ were excluded from calculations. Refinement was done by full-matrix least-squares based on F^2 using the SHELX-93 package [15]. All non-H atoms were treated anisotropically. Hydrogen atoms were included but not refined. An extinction correction was applied. Lorentz, polarization and absorption corrections were made [16]. Crystal size: 0.30 × 0.27 × 0.12 mm. T_{min} and T_{max} were 0.267 and 0.654, respectively. Scattering factors were taken from International Tables for X-ray Crystallography [17].

Table 1. Crystal data and structure refinement

Empirical formula	$C_{56}H_{43}Br_5N_7ORu_2$
fw	1431.86
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
a (Å)	12.011(1)
b (Å)	13.154(3)
c (Å)	20.124(4)
α (°)	74.84(2)
β (°)	84.30(1)
γ (°)	68.82(1)
V (Å^3)	2861.5(9)
Z	2
ρ (calc) (mg m^{-3})	1.652
T (K)	293 ± 1
Radiation, λ (Å)	Mo-K_α, 0.71069
μ (cm^{-1})	40.73
θ range (°)	1.71–22.45
No. of collected reflections	3772
No. of reflections for calc.	3760
$R_1{}^a$	0.036
$wR_2{}^b$	0.091

[a] $R_1 = \Sigma(|F_0| - |F_c|)/\Sigma|F_0|$.

[b] $wR_2 = [\Sigma w(F_0{}^2 - F_c{}^2)^2/\Sigma wF_0{}^4]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (°)

Ru(1)—Br(1)	2.525(2)	Ru(1)—N(1)	2.005(9)
Ru(1)—N(2)	2.004(9)	Ru(1)—N(3)	2.007(8)
Ru(1)—N(4)	2.013(8)	Ru(1)—N(5)	2.017(8)
Ru(2)—Br(2)	2.495(1)	Ru(2)—Br(3)	2.490(1)
Ru(2)—N(6)	2.008(8)	Ru(3)—Br(4)	2.491(1)
Ru(3)—Br(5)	2.485(2)	Ru(3)—N(7)	1.99(1)
N(1)—C(1)	1.13(2)	N(2)—C(8)	1.11(2)
N(3)—C(15)	1.13(1)	N(4)—C(22)	1.12(1)
N(5)—C(29)	1.13(1)	N(6)—C(36)	1.14(1)
N(7)—C(43)	1.12(2)	C(1)—C(2)	1.45(2)
C(2)—C(3)	1.38(1)	C(2)—C(7)	1.40(2)
Br(1)—Ru(1)—N(1)	177.4(2)	Br(1)—Ru(1)—N(2)	91.8(3)
Br(1)—Ru(1)—N(3)	85.9(3)	Br(1)—Ru(1)—N(4)	92.4(3)
Br(1)—Ru(1)—N(5)	90.1(3)	N(1)—Ru(1)—N(2)	87.7(3)
N(1)—Ru(1)—N(3)	91.6(3)	N(1)—Ru(1)—N(4)	88.2(4)
N(1)—Ru(1)—N(5)	92.4(3)	N(2)—Ru(1)—N(3)	91.2(3)
N(2)—Ru(1)—N(4)	175.6(4)	N(2)—Ru(1)—N(5)	91.0(3)
N(3)—Ru(1)—N(4)	90.6(3)	N(3)—Ru(1)—N(5)	175.5(4)
N(4)—Ru(1)—N(5)	87.4(3)	Br(2)—Ru(2)—Br(3)	90.00(4)
Br(2)—Ru(2)—N(6)	91.5(3)	Br(2)—Ru(2)—N(6)	88.5(3)
Br(3)—Ru(2)—N(6)	91.7(2)		

RESULTS AND DISCUSSION

The reaction between $RuBr_3 \cdot xH_2O$ and benzaldehyde oxime proceeds rapidly on heating the reagents at 60°C in aqueous 6 M HBr. One product of the reaction, the mixed-valence nitrile complex $[RuBr(N{\equiv}CPh)_5][RuBr_4(N{\equiv}CPh)_2]$ was extracted into chloroform and, after removal of the solvent, obtained in 23% yield. The aqueous solution remaining after the extraction contains a mixture of as yet unidentified ruthenium species. The chloride analog of $[RuBr(N{\equiv}CPh)_5][RuBr_4(N{\equiv}CPh)_2]$ has been earlier prepared in the reaction of $RuCl_3 \cdot xH_2O$ with benzonitrile in methanol [18].

The dehydration is metal-assisted: GC-MS and TLC monitoring of a blank reaction between $PhC(H){=}NOH$ and 6 M HBr shows no evidence of PhCN, although some $PhC(H){=}O$ has been detected. The latter product is apparently due to partial hydrolysis of benzaldehyde oxime which results in the formation of benzaldehyde and $NH_3OH^+Br^-$. Both these species might reduce Ru^{III} to Ru^{II}; reduction of ruthenium(III) complexes by hydroxylamine is known [19]. We assume that the reaction proceeds *via* N-coordination of the oxime to the metal ion which promotes increased unsaturation at the bonded nitrogen atoms—a phenomenon generally attributed to back-bonding from the 4*d* orbitals of Ru^{II} or Ru^{III} to the empty π^* orbitals on sp^2- or sp-hybridized nitrogen—thus facilitating the dehydration. The high stability of the ruthenium–nitrile bond so formed is well-documented [20].

The ruthenium compound $[RuBr(N{\equiv}CPh)_5][RuBr_4(N{\equiv}CPh)_2]$ upon recrystallization from benzyl alcohol forms the monosolvate. The structure of $[RuBr(N{\equiv}CPh)_5][RuBr_4(N{\equiv}CPh)_2] \cdot PhCH_2OH$ has been verified by single-crystal X-ray diffraction (Fig. 1). The complex consists of two discrete ions, i.e. the cation $[RuBr(N{\equiv}CPh)_5]^+$ and the anion $[RuBr_4(N{\equiv}CPh)_2]^-$; the presence of these ions was also confirmed by FAB mass spectrometry. Two symmetrically independent anions $[RuBr_4(N{\equiv}CPh)_2]^-$ are located on centers of symmetry, while a cation $[RuBr(N{\equiv}CPh)_5]^+$ is found in a general position. Two molecules of benzyl alcohol (omitted in Fig. 1 for simplicity) are also situated in different centrosymmetric positions.

In both ions, all benzonitrile ligands are end-on coordinated to the ruthenium centers. The $Ru{—}N{\equiv}C$ angles vary from 167(1) [Ru(1)—N(4)—C(22)] to 177.7(9)° [Ru(3)—N(7)—C(43)] and this indicates that the $Ru{—}N{\equiv}C$ groups are close to linear. As expected [21], the $N{\equiv}C{—}C$ angles [175.4(9)–179(1)°] deviate to a much lesser extent from linearity. The $Ru^{II}{—}N$ [22], $Ru^{III}{—}N$ [23], $Ru^{II}{—}Br$ [24], $Ru^{III}{—}Br$ [25] and $C{\equiv}N$ [21,22,26] bond lengths are of normal values.

In conclusion, it is worthwhile to mention that (i) as a rule, syntheses of oximes from aldehydes and hydroxylamine are much easy than those of the corresponding nitriles [27]. Thus, the Ru-assisted dehydration of oximes may be valuable in the synthesis of complexes with difficult-to-obtain and/or commercially unavailable nitriles. These reactions are under investigation in our group. (ii) It is well-documented [28] that in the vast majority of cases the metal centers in mixed-valence Ru^{III}/Ru^{II} species are linked by bridging ligands. To the best of our knowledge, the mixed-valence compounds $[RuX(N{\equiv}CPh)_5][RuX_4(N{\equiv}CPh)_2]$ (X = Cl [18], Br) are rare examples of

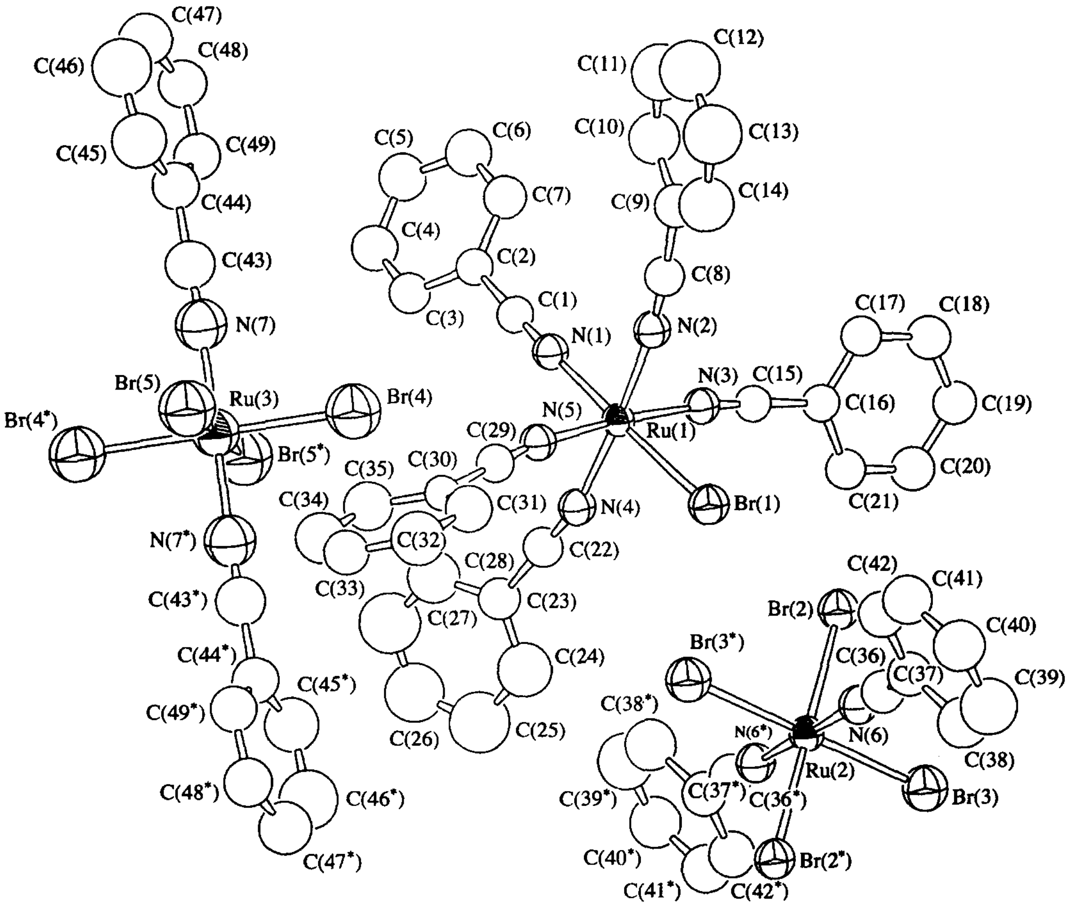

Fig. 1. ORTEP plot of $[RuBr(N{\equiv}CPh)_5][RuBr_4(N{\equiv}CPh)_2]$ with atomic numbering. Two $[RuBr_4(N{\equiv}CPh)_2]^-$ anions, each of 50% occupancy, are shown.

discrete, ionic Ru^{III}/Ru^{II} complexes. Previously, only the hexacyanide–ammine ion-pairs, $[Ru^{III}L(NH_3)_5||Ru^{II}(CN)_6]^-$ (L = nitrogen heterocycle, e.g. pyridine), have been prepared and characterized [29].

Note added in proof—Since this paper was submitted for publication, we have found that the yield of the reaction can be increased up to *ca* 60% if the mixture is heated at 80°C in an open beaker for 20 min, cooled to room temperature and left to stand at 20–25°C for 2 days followed by filtration of the mixed-valence compound.

Acknowledgments—The authors are grateful to the Russian Fund of Basic Research for financial support. The authors are much obliged to Professors M. Calligaris, J. Winkler and E. Zangrando for helpful information related to this work and to Professor J. A. Davies for valuable suggestions.

Supplementary material. Tables of crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, observed and calculated structure factors.

REFERENCES

1. Kukushkin, V. Yu., Tudela, D. and Pombeiro, A. J. L., *Coord. Chem. Rev.* 1996, **156**, 333, and references therein.
2. Olah, G. A., Narang, S. C. and Garcia-Luna, A., *Synthesis* 1980, 659.
3. Olah, G. A. and Vankar, Y. D., *Synthesis* 1978, 702.
4. Jursic, B., *Synth. Commun.* 1989, **19**, 689.
5. Kim, S. and So, Y. K., *Bull. Korean Chem. Soc.* 1987, **8**, 50.
6. Guengerich, C. P. and Schug, K., *Inorg. Chem.* 1983, **22**, 181.
7. Daniel, T., Knaup, W., Dziallas, M. and Werner, H., *Chem. Ber.* 1993, **126**, 1981.
8. Czarkie, D. and Shvo, Y., *J. Organomet. Chem.* 1985, **280**, 123.
9. Lalia-Kantouri, M. and Hartophylles, M., *Thermochim. Acta* 1993, **224**, 203.
10. Olczak-Kobza, M., *Thermochim. Acta* 1988, **133**, 347.
11. (a) Kukushkin, V. Yu., Belsky, V. K., Aleksandrova, E. A., Konovalov, V. E. and Kirakosyan, G. A., *Inorg. Chem.* 1992, **31**, 3836; (b) Kukushkin, V. Yu., Belsky, V. K. and Tudela,

D., *Inorg. Chem.* 1996, **35,** 510; (c) Kukushkin, V. Yu., Tudela, D., Izotova, Y. A., Belsky, V. K. and Stash, A. I., *Inorg. Chem.* 1996, **35,** 4926.

12. (a) Kukushkin, V. Yu., Aleksandrova, E. A. and Kukushkin, Yu. N., *Zh. Obsch. Khim.* 1995, **65,** 1937; (b) Svensson, P., Lövqvist, K., Kukushkin, V. Yu. and Oskarsson, Å., *Acta Chem. Scand.* 1995, **49,** 72; (c) Kukushkin, V. Yu., Oskarsson, Å. and Elding, L. I., *Inorg. Synth.* 1995, **31,** 276; (d) Kukushkin, V. Yu. and Tkachuk, V. M., *Z. Anorg. Allg. Chem.* 1992, **613,** 123.
13. Strel'tsov, V. A. and Zavodnik, V. E., *Kristallografia* 1989, **34,** 1369.
14. Sheldrick, G. M., *SHELXTL User Manual,* Revision 3. Nicolet XRD Corporation Cupertino, CA, U.S.A., 1981.
15. Sheldrick, G. M., *SHELX*-93. University of Göttingen, Germany, 1993.
16. Axelrud, L. G., Grin, Yu. N., Zavalii, P. Yu., Pecharsky, V. K. and Fundamensky, V. S., CSD-universal program package for single crystal and/or powder structure data treatment. Collected Abstracts, *XII-th European Crystallographic Meeting.* Moscow, August 1989. USSR Academy of Sciences, Moscow, 1989, p. 155.
17. *International Tables for X-ray Crystallography,* Vol. IV, Kynoch Press, Birmingham, U.K., 1974.
18. (a) Dehand, J. and Rosé, J., *J. Chem. Res.* (*S*) 1979, 155; (b) Dehand, J. and Rosé, J., *J. Chem. Res.* (*M*) 1979, 2167.
19. Aoyagi, K., Mukaida, M., Kakihana, H. and Shimizu, K., *J. Chem. Soc., Dalton Trans.* 1985, 1733.
20. (a) Davies, J. A., Hockensmith, C. M., Kukushkin, V. Yu. and Kukushkin, Yu. N., *Synthetic Coordination Chemistry: Principles and Practice.* World Scientific: Singapore–New Jersey, 1996, p. 95; (b) Duff, C. M. and Heath, G. A., *Inorg. Chem.* 1991, **30,** 2528; (c) Duff, C. M. and Heath, G. A., *J. Chem. Soc., Dalton Trans.* 1991, 2401.
21. Endres, H., in *Comprehensive Coordination Chemistry,* ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Vol. 2. Pergamon Press, Oxford, 1987, p. 262.
22. (a) Zhilyaev, A. N., Fomina, T. A., Kuzmenko, I. V., Katser, S. B. and Baranovskii, I. B., *Zh. Neorg. Khim.* 1990, **35,** 2253; (b) Luginbuhl, W., Ludi, A., Baselli, A. and Bürgi, H.-B., *Acta Cryst.* 1989, **C45,** 1428; (c) Bown, M., Fontaine, X. L. R., Greenwood, N. N., Kennedy, J. D. and Thornton-Pett, M., *J. Chem. Soc., Dalton Trans.* 1987, 1169.
23. (a) Hage, R., Prins, R., de Graaff, R. A. G., Haasnoot, J. G., Reedijk, J. and Vos, J. G., *Acta Cryst.* 1988, **C44,** 56; (b) Crutchley, R. J., McCaw, K., Lee, F. L. and Gabe, E. J., *Inorg. Chem.* 1990, **29,** 2576; (c) Syamala, A., Das, B. K. and Chakravarty, A. R., *Polyhedron* 1992, **11,** 335; (d) Das, B. K. and Chakravarty, A. R., *Inorg. Chem.* 1990, **29,** 2078; (e) Duff, C. M., Heath, G. A. and Willis, A. C., *Acta Cryst.* 1990, **C46,** 2320.
24. Alessio, E., Mestroni, G., Nardin, G., Attia, W. M., Calligaris, M., Sava, G. and Zorzet, S., *Inorg. Chem.* 1988, **27,** 4099.
25. (a) James, B. R., Dolphin, D., Leung, T. W., Einstein, F. W. B. and Willis, A. C., *Can. J. Chem.* 1984, **62,** 1238; (b) Appleby, D., Crisp, R. I., Hitchcock, P. B., Hussey, C. L., Ryan, T. A., Sanders, J. R., Seddon, K. R., Turp, J. E. and Zora, J. A., *J. Chem. Soc., Chem. Commun.* 1986, 483; (c) Appleby, D., Hitchcock, P. B., Seddon, K. R., Turp, J. E., Zora, J. A., Hussey, C. L. and Sanders, J. R., *J. Chem. Soc., Dalton Trans.* 1990, 1879; (d) Tomizawa, H., Harada, K., Miki, E., Mizumachi, K., Ishimori, T., Urushiyama, A. and Nakahara, M., *Bull. Chem. Soc. Jpn* 1993, **66,** 1658; (e) Champness, N. R., Levason, W., Pletcher, D. and Webster, M., *J. Chem. Soc., Dalton Trans.* 1992, 3243.
26. Rochon, F. D., Melanson, R., Thouin, E., Beauchamp, A. L. and Bensimon, C., *Can. J. Chem.* 1996, **74,** 144.
27. Grashey, R., in *Comprehensive Organic Synthesis,* ed. B. M. Trost, Vol. 6. Pergamon Press, Oxford, 1991, p. 225.
28. (a) Ward, M. D., *Chem. Soc. Rev.* 1995, **24,** 121; (b) Bardwell, D. A., Horsburgh, L., Jeffery, J. C., Joulié, L. F., Ward, M. D., Webster, I. and Yellowlees, L. J., *J. Chem. Soc., Dalton Trans.* 1996, 2527, and refs therein.
29. (a) Curtis, J. C. and Meyer, T. J., *Inorg. Chem.* 1982, **21,** 1562; (b) Brunschwig, B. S., Ehrenson, S. and Sutin, N., *J. Phys. Chem.* 1986, **90,** 3657.