Radical substitution on a thioester by a methyl radical generated from methyl(L)cobaloxime

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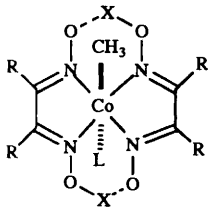
Photolysis of methyl(L)cobaloxime **1**, Me(L)[Co], in the presence of *S*-(4-chlorophenyl) thioacetate **5**, yielded 4-chlorophenyl methyl sulfide **6**. The reactivity of the methyl(L)cobaloxime with the thioester increases when the cobaloxime has a *trans* phosphine ligand (L) of larger steric requirement or a 4-substituted pyridine ligand (L) of lower basicity. Methyl(L)BF_2-cobaloxime **2**, methyl(L)tetraphenylcobaloxime **3** and methyl(L)BF_2-tetraphenylcobaloxime **4** having electronegative or bulky equatorial ligands lose their reactivity with the thioester. The generation of the methyl radical from cobaloxime **2** is more efficient than from cobaloxime **1** in spite of its poor reactivity with the thioester. These features of the reaction are accounted for by 'the effective concentration of the out-of-cage methyl radical' and 'the coordinative interaction of the thioester with the cobalt(II) complex'.

Introduction

In the last few years there has been growing interest in radical substitution on sulfur on both theoretical[1] and experimental[2] grounds. We have been studying radical substitution on thioesters[3] in connection with model studies of enzymic radical rearrangements.[4] Alkyl radical substitution on sulfur takes place intramolecularly[3a-c] as well as intermolecularly[3d,e] and with sulfide,[5] sulfoxide[2c,6] disulfide,[7] thiosulfonate[8] and sulfinyl ester[9] substrates.

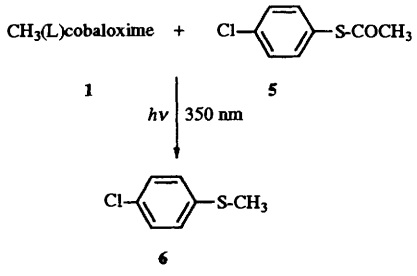
We proposed the possible involvement of cobalt(II) complexes in these substitutions based on product analyses[3a,c] and an ESR study.[10] The ESR study showed the coordinative interaction between a thioester and a cobalt(II) complex. The effect of a *trans* ligand on the stability of an alkyl–cobalt bond has been thoroughly investigated,[11] and the following general feature has been clarified; that is, an alkyl–cobalt bond is destabilised by bulky phosphine ligands and stabilised by more basic pyridines. With those facts to hand, we studied the effect of the ligand of methylbis(dimethylglyoximato)(ligand)-cobalt(III), methyl(L)cobaloxime or Me(L)[Co] hereafter, and its derivatives on the radical substitution of a thioester.



1: X = H R = Me
2: X = BF_2 R = Me
3: X = H R = Ph
4: X = BF_2 R = Ph

Methyl(L)cobaloximes **1** were photolysed by a 350 nm lamp in the presence of *S*-(4-chlorophenyl) thioacetate **5** in benzene (L = phosphines) or acetonitrile (L = pyridines) under anaerobic conditions. Essentially no exchange took place between the ligand and the thioester under these reaction conditions. The reactions were stopped at an early stage or before completion, while the starting materials still persisted, to estimate relative reactivities. The only isolable organic product was 4-chlorophenyl methyl sulfide **6** (Scheme 1).

Results are summarised in Table 1. The time-course of the reaction was not traced due to the opacity of the reaction mixture at a later stage of the photolysis. The product **6**, however, is stable under the photolysis conditions. The yields in



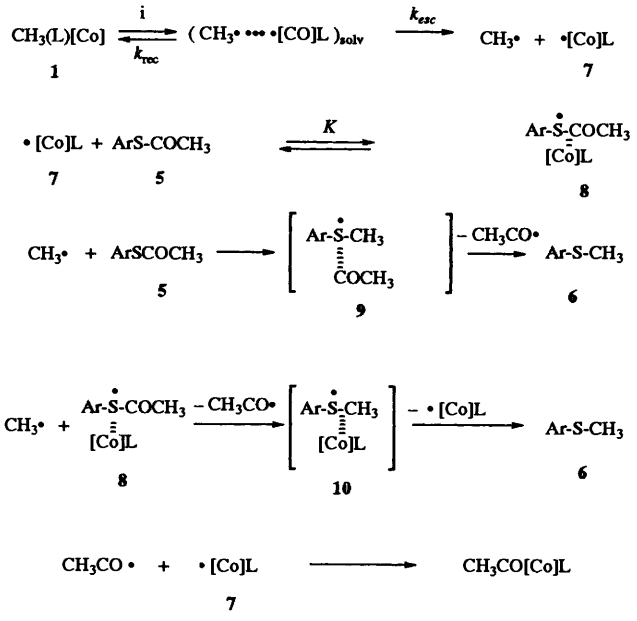
Scheme 1 *Conditions: hν* (350 nm)

Table 1 Photolysis of methyl(L)cobaloxime **1** in the presence of *S*-(4-chlorophenyl) thioacetate **5**[a-c]

Cobaloxime	L	Yield (%) of **6**	Cone angle (°)[12]	pK_a[12,13]
1a	P(c-hex)$_3$	25	173	9.7
1b	PPh_3	25	159	2.7
1c	PPh_2Bu	5	140	5.0
1d	PBu_3	2	129	8.4
1e	4-cyanopyridine	36		1.9
1f	Py	29		5.2
1g	4-Bu^{t}pyridine	23		5.9
2a	4-cyanopyridine	1.4		1.9
2b	Py	0.4		5.2
2c	4-Bu^{t}pyridine	1.1		5.9

[a] Me(phosphines)[Co] **1a–1d**, 3.0 mmol dm^{-3}; thioester **5**, 20.0 mmol dm^{-3} in benzene. Irradiation, 24 h. [b] Me(pyridines)[Co] **1e–1g**, 3.0 mmol dm^{-3}; thioester **5**, 20.0 mmol dm^{-3} in acetonitrile. Irradiation, 20 h. [c] Me(pyridines)BF_2-[Co] **2a–2c**, 3.0 mmol dm^{-3}; thioester **5**, 20.0 mmol dm^{-3} in acetonitrile. Irradiation, 40 h.

Table 1 indicate the rank of reactivity but not the relative rates, and therefore the following discussions must remain qualitative while being meaningful because all irradiations of the same series of cobaloximes were carried out under identical conditions. As seen in Table 1, methyl(L)cobaloximes **1a–1d** having a bulky phosphine ligand showed higher reactivity. Some electronic effect is envisaged because tricyclohexylphosphine and triphenylphosphine showed nearly the same reactivity irrespective of the difference in steric bulkiness as



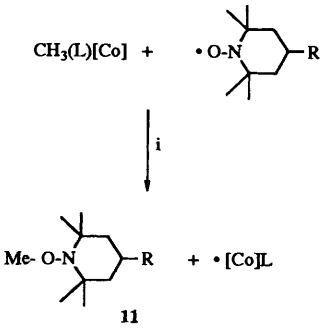
Scheme 2 *Conditions:* i, *hv*

judged from the cone angles.[12] Steric bulkiness is essentially the same within 4-substituted pyridines, and the reactivity of methyl(pyridines)cobaloxime **1e–1g** depends on the basicity of the pyridines.[13]

Methyl(pyridines)BF_2-cobaloxime **2a–2c** yielded less than 1.5% of sulfide **6** even after prolonged irradiation, and it is notable that the electronegative planar ligand in radicals **7** reduced the reactivity with the thioester.

Photolysis of methyl(L)cobaloxime causes cleavage of the carbon–cobalt bond to give a pair of methyl and cobaloxime(II) radicals.[14] The cobaloxime(II) radical **7** exists in equilibrium with the thioester–cobalt complex **8** as evidenced by an ESR study.[10] The methyl radical can attack thioester **5** directly or the complexed thioester **8** to give the aryl methyl sulfide **6** through sulfuranyl radicals **9** or **10** as intermediates or transition states (Scheme 2). The acetyl radical and cobaloxime(II) radical **7** couple to form acetyl(L)cobaloxime though we did not try to isolate the cobaloxime. Its photolysis, if any, should not interfere with the present results, because *S*-(4-chlorophenyl) thiopivalate instead of acetate gave the same results. Thus we can exclude the generation of the methyl radical by photolysis of the resulting acetyl(L)cobaloxime. Coordination of the thioester with the cobaloxime(II) complex generates a spin density on the sulfur (see structure **8**) and the sulfur of the thioester is expected to become more radicophilic. These schemes indicate that the formation of sulfide **6** is influenced both by the effective concentration of the out-of-cage methyl radical and the formation of complex **8** between the thioester and the cobaloxime(II) radical.

2,2,6,6-Tetramethylpiperidin-1-oxyl (TEMPO) is a good alkyl radical trap in the reaction of the alkyl–cobalt complex because the redox and the coordination between TEMPO and cobalt(II) complexes are not important.[15] The effective concentration of the out-of-cage methyl radical from methyl(L)-cobaloxime **1** can be estimated by diffusion-controlled trapping by TEMPO (Scheme 3).[15] Photolyses of methyl(L)cobaloximes **1** and **2** in the presence of 10^{-3}–10^{-2} mol dm^{-3} TEMPO gave methyl-TEMPO **11** in constant yields due to the complete scavenging of the out-of-cage methyl radical. Therefore the relative yield of methyl-TEMPO **11** is a reasonable reflection of the effective concentration of the out-of-cage methyl radical in the photolysis system. The fast formation of the methyl-TEMPO, compared with the rather slow reaction of the methyl



Scheme 3 *Conditions:* i, *hv*

Table 2 Photolysis of methyl(L)cobaloxime **1** and methyl(L)BF_2-cobaloxime **2** in the presence of TEMPO and 4-benzoyloxy-TEMPO[a–c]

Cobaloxime	L	Yield (%) of **11**
1a	$P(c\text{-hex})_3$	67
1b	PPh_3	67
1c	PPh_2Bu	39
1d	PBu_3	28
1e	4-cyanopyridine	55
1f	Py	49
1g	4-Bu^{t}pyridine	38
2a	4-cyanopyridine	91
2b	Py	89
2c	4-Bu^{t}pyridine	71

[a] Me(phosphines)[Co] **1a–1d**, 6.0 mmol dm^{-3}; TEMPO, 90.0 mmol dm^{-3} in benzene. Irradiation, 4 h. [b] Me(pyridines)[Co] **1e–1g**, 3.0 mmol dm^{-3}; 4-benzoyloxy-TEMPO, 10.0 mmol dm^{-3}. Irradiation, 1.5 h. [c] Me(pyridines)BF_2-[Co] **2a–2c**, 3.0 mmol dm^{-3}; 4-benzoyloxy-TEMPO, 10.0 mmol dm^{-3}. Irradiation, 0.5 h.

radical with the thioester, suggests that the recombination of the out-of-cage radical pair as well as the in-cage recombination is a major process in the absence of TEMPO.

The yield of methyl-TEMPO **11** from methyl(phosphine)-cobaloximes **1a–1d** decreased in the order: L = $P(c\text{-hex})_3 \approx PPh_3$, PPh_2Bu and PBu_3 (Table 2), where c-hex is cyclohexyl. Thus, the reactivities of cobaloximes **1a–1d** with thioester **5** and TEMPO have parallel trends, and seem to be controlled by the bulkiness of the phosphines. On the other hand, the reactivities of methyl(pyridine)cobaloximes **1e–1g** seem to be influenced by the basicity of the *trans* ligand. Thus, methyl-(4-cyanopyridine)cobaloxime **1e** showed higher reactivity than did methyl-(4-*tert*-butylpyridine)cobaloxime **1g** both with the thioester and with a TEMPO derivative.

These results indicate that the reactivity of methyl(L)cobaloxime **1** is influenced by the steric bulkiness and basicity of the *trans* ligand L. We have no definite explanation for this result, but it is similar to the trend which exists between *trans* ligands and cobalt–alkyl bond energies[16] as well as the photolysis rate, elegantly shown by the racemisation of chiral alkyl(L)cobaloximes.[17] The effective concentration of the out-of-cage methyl radical is determined by the relative rate of the recombination (k_{rec}) and the escape rate (k_{esc}) from the solvent cage (Scheme 2). The former rate must be related to the cobalt–alkyl bond energy and is expected to be reduced by bulky or less basic *trans* ligands (L). These ligands, therefore, raise the reactivity by increasing the concentration of the out-of-cage methyl radical. Methyl(pyridines)BF_2-cobaloximes **2a–2c** gave a methyl-TEMPO derivative much more efficiently than did methyl(pyridines)cobaloximes **1e–1g** (Table 2), and hence the effective concentration of the out-of-cage methyl radical from cobaloximes **2** must be higher than that of the methyl radical from cobaloximes **1**. Nevertheless, the reactivity of cobaloximes **2** towards the thioester is extremely poor. This loss of reactivity

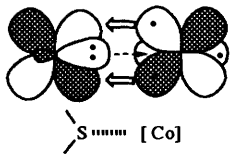


Fig. 1 Bonding interaction of Co–S

of cobaloximes **2** with the thioester can be understood by considering that the major path is the substitution on the cobalt-coordinated thioester **8** rather than the direct substitution on the thioester **5** (Scheme 3).

The nature of the bonding in the cobalt–sulfur complex **8** is proposed to be more back-donative (Fig. 1).[10] The back donation from cobalt to sulfur is diminished by an electronegative BF_2 group, as evidenced by the increase in the $Co^{II/III}$ redox potential,[18] and effective coordination between cobalt(II) and the thioester cannot be expected. This concept suggests the reduced reactivity of methyl(pyridine)tetraphenylcobaloxime **3**[19] and methyl(pyridine)BF_2-tetraphenylcobaloxime **4** which cannot be coordinated efficiently with the thioester due to the steric hindrance exerted by the four tilted phenyl groups.[10,19]

Photoreaction of cobaloximes **2b**, **3** (L = Py), and **4** (L = Py) with *S*-(4-chlorophenyl) thioacetate **5** in acetonitrile gave sulfide **6** in only 1, 9, and 1% yield, respectively. Thus, electronegative or sterically bulky equatorial ligands remarkably decrease the reactivity of the methyl(L)cobaloximes with the thioester. This result supports the proposed cobaloxime-mediated radical substitution on sulfur as shown in Scheme 2.

In conclusion the relative reactivities of methyl(L)-cobaloximes in radical substitution on the thioester is controlled by two factors; (a) the effective concentration of the out-of-cage methyl radical and (b) the coordination of the thioester with the cobaloxime(II) radical.

Experimental

Mps were measured on a Yamato MP-21 apparatus and no correction was made. 90 MHz ^1H NMR spectra were recorded on a Hitachi R-90 spectrometer using TMS as an internal standard in $CDCl_3$ or CD_2Cl_2 solution. *J* Values are recorded in Hz. Microanalyses were carried out on a Perkin-Elmer 2400II elemental Analyzer.

Syntheses of methyl(L)cobaloximes 1

Methyl(L)cobaloximes **1a** [L = P(c-hex)$_3$], **1c** (L = PPh_2Bu), **1d** (L = PBu_3)[20] and **1e** (L = 4-cyanopyridine)[21] were prepared by ligand exchange of methyl(Me_2S)cobaloxime[21] in refluxing benzene. Methyl(L)cobaloximes **1b** (L = PPh_3),[20] **1f** (L = Py)[22] and **1g** (L = 4-Bu^{t}pyridine)[23] were prepared directly from $CoCl_2 \cdot 6H_2O$, and the respective ligands under reduction conditions.[22] Satisfactory elemental analyses and spectral data were obtained on all known cobaloximes (**1b**, **1d**, **1e**, **1f** and **1g**).

Cobaloxime **1a**,[24] mp 187.0–188.0 °C (decomp.); δ_H(90 MHz; $CDCl_3$) 0.84 (3 H, d, J_P 3.6), 0.87–2.03 (33 H, m), 2.20 (12 H, d, J_P 3.0) and 18.46 (2 H, br s) (Found: C, 55.2; H, 8.75; N, 9.6. $C_{27}H_{50}CoN_4O_4P$ requires C, 55.47; H, 8.62; N, 9.58%).

Cobaloxime **1c**, mp 150 °C (decomp.); δ_H(90 MHz; $CDCl_3$) 0.80 (3 H, t, J_P 6.0), 0.90–2.60 (6 H, m), 1.06 (3 H, d, J_P 4.0), 1.82 (12 H, d, J_P 3.4), 7.02–7.35 (10 H, m) and 18.08 (2 H, br s) (Found: C, 55.0; H, 6.7; N, 10.2. $C_{25}H_{36}CoN_4O_4P$ requires C, 54.95; H, 6.64; N, 10.25%).

Syntheses of methyl(L)BF_2-cobaloximes 2

Methyl-(4-cyanopyridine)BF_2-cobaloxime **2a** was prepared by the ligand exchange of methyl(H_2O)BF_2-cobaloxime[20] with 4-cyanopyridine in dichloromethane at ambient temp. Methyl(L)BF_2-cobaloxime **2b** (L = Py) and **2c** (L = 4-Bu^t pyridine) were prepared by treatment of cobaloxime **1f** and **1g**, respectively, with BF_3–diethyl ether in dichloromethane at ambient temp. as described for compound **2b**.[20]

Cobaloxime **2a**, mp 218.0–218.5 °C (decomp.); δ_H(90 MHz; $CDCl_3$) 1.41 (3 H, s), 2.35 (12 H, s), 7.62 (2 H, dd, *J* 4.9 and 1.3) and 8.20 (2 H, dd, *J* 4.9 and 1.4) (Found: C, 35.75; H, 3.8; N, 16.7. $C_{15}H_{19}B_2CoF_4N_6O_4$ requires C, 35.8; H, 3.73; N, 16.76%).

Cobaloxime **2c**, mp 212.0–213.0 °C (decomp.); δ_H(90 MHz; CD_2Cl_2) 1.29 (9 H, s), 1.40 (3 H, s), 2.35 (12 H, s), 7.30 (2 H, dd, *J* 5.9 and 1.6) and 8.01 (2 H, dd, *J* 5.9 and 1.6) (Found: C, 40.1; H, 5.15; N, 13.1. $C_{18}H_{28}B_2CoF_4N_5O_4$ requires C, 40.41; H, 5.28; N, 13.09%).

Syntheses of methyl(pyridine)tetraphenylcobaloxime 3 and methyl(pyridine)BF_2-tetraphenylcobaloxime 4

Cobaloxime **3** was prepared by the reported method[19] and was identified by elemental analysis and spectral data. Cobaloxime **4** was prepared by treatment of cobaloxime **3** (1.0 g, 1.6 mmol) with BF_3–diethyl ether (1.0 cm^3; 8.1 mmol) in dichloromethane (10 cm^3) at ambient temp. The resulting precipitate was dissolved by addition of dichloromethane (180 cm^3), and the solution was washed with water three times, and dried over sodium sulfate. After removal of solvent, the residue was added to dichloromethane (30 cm^3) containing pyridine (0.2 cm^3, 2.6 mmol), and the mixture was stirred for 1 h. The product obtained after removal of solvent was recrystallised from dichloromethane–diethyl ether using diffusional mixing of the solvents.

Cobaloxime **4** mp 219.0–220.0 °C (decomp.); δ_H(90 MHz; CD_2Cl_2) 2.09 (3 H, s), 6.95–7.68 (20 H, m), 7.54 (2 H, dd, *J* 6.6 and 6.5), 7.90 (1 H, tt, *J* 6.5 and 1.5) and 8.53 (2 H, dd, *J* 6.6 and 1.5) (Found: C, 55.8; H, 4.0; N, 9.7. $C_{34}H_{28}B_2CoF_4N_5O_4$ requires C, 56.16; H, 3.88; N, 9.65%).

Photochemical reaction of methyl(L)cobaloximes 1a–1g and methyl(L)BF_2-cobaloximes 2a–2c with *S*-(4-chlorophenyl)-thioacetate 5

To a solution of the thioacetate **5** (20 mmol dm^{-3}) in benzene or acetonitrile was added one of the cobaloximes **1a–1g** or **2a–2c**, 3.0 mmol dm^{-3}). The solutions (14 cm^3 each) containing different cobaloximes were degassed by bubbling argon through syringe needles under ultrasonic irradiation. The degassed solutions were irradiated under identical conditions with a merry-go-round-type photoreactor (Rayonett RPR-100) equipped with 350 nm lamps (RPR-3500A). The reaction mixtures were concentrated and the polar degradation products as well as the persisting cobaloximes were removed by chromatography on silica gel eluted with benzene or hexane–dichloromethane (65:35). The eluents were adjusted to the same volume and were analysed by gas chromatography on an SE-30 on Chromosorb-W column or a semicapillary column coated with SE-30 (N_2). The analyses showed only one product in addition to the starting material. The product was identified as 4-chlorophenyl methyl sulfide **6** by comparison of the retention time and mass spectrum with those of an authentic sample.[25] Relative yields of the sulfide **6** were determined by the gas chromatography using 1,4-dichlorobenzene as an internal standard. The reaction conditions are recorded as footnotes to Tables 1 and 2.

Photochemical reaction of methyl(L)cobaloximes 1a–1g, methyl(pyridine)BF_2-cobaloximes 2a–2c, methyl(pyridine)-tetraphenylcobaloxime 3 and methyl(pyridine)BF_2-tetraphenyl-cobaloxime 4 with TEMPO or 4-benzoyloxy-TEMPO

The mixtures of the cobaloximes and TEMPOs were irradiated in the same manner as recorded for the photoreactions of the

cobaloxime with the thioester. The reaction conditions are recorded as footnotes to Table 2. The products, methyl-TEMPO **11a**[26] and 4-benzoyloxy(methyl)TEMPO **11b**,[27] were identified by comparison with authentic samples and were determined by the same procedure as that recorded for the photoreaction with the thioester.

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References

1 J. A. Franz, D. H. Roberts and K. F. Ferris, *J. Org. Chem.*, 1987, **52**, 2256; K. F. Ferris and J. A. Franz, *J. Org. Chem.*, 1992, **57**, 777; J. E. Lyons and C. H. Schiesser, *J. Organomet. Chem.*, 1992, **437**, 165; *J. Chem. Soc., Perkin Trans. 2*, 1992, 1655.
2 (*a*) P. Beak and T. A. Sullivan, *J. Am. Chem. Soc.*, 1982, **104**, 4450; (*b*) J. E. Baldwin, R. M. Adlington and M. J. Bohlmann, *J. Chem. Soc., Chem. Commun.*, 1985, 357; (*c*) A. L. J. Beckwith and D. R. Boate, *J. Chem. Soc., Chem. Commun.*, 1986, 189; (*d*) M. C. Fong and C. H. Schiesser, *Aust. J. Chem.*, 1992, **45**, 475.
3 (*a*) M. Tada, K. Inoue and M. Okabe, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 1420; *Chem. Lett.*, 1986, 703; (*b*) M. Tada, K. Inoue, K. Sugawara, M. Hiratsuka and M. Okabe, *Chem. Lett.*, 1985, 1821; (*c*) M. Tada, T. Nakamura and M. Matsumoto, *Chem. Lett.*, 1987, 409; 1988, 199; *J. Am. Chem. Soc.*, 1988, **110**, 4647; (*d*) M. Tada, T. Uetake and M. Matsumoto, *J. Chem. Soc., Chem. Commun.*, 1990, 1408; (*e*) M. Tada, T. Hirokawa and T. Tohma, *Chem. Lett.*, 1991, 857.
4 B_{12}, ed. D. Dolphin, Wiley, New York, 1982.
5 A. L. J. Beckwith and D. R. Boate, *Tetrahedron Lett.*, 1970, 3677; 1985, **26**, 1761; V. Patel and G. Pattenden, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2703; D. J. Coveney, V. Patel, G. Pattenden and D. M. Thompson, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2721.
6 M. Tada and H. Nakagiri, *Tetrahedron Lett.*, 1992, **33**, 6657.
7 W. A. Pryer and K. Smith, *J. Am. Chem. Soc.*, 1970, **92**, 2731; R. N. Haszeldine, R. B. Rigby and A. E. Tipping, *J. Chem. Soc., Perkin Trans. 1*, 1972, 159; G. Russel and S. V. Hulkarni, *J. Org. Chem.*, 1993, **58**, 2678.
8 A. C. Serra and M. M. da Silva-Correa, *Tetrahedron Lett.*, 1991, **32**, 6653.
9 A. Arbertazzi, R. Leardini, G. F. Tundo and G. Zanardi, *J. Org. Chem.*, 1984, **49**, 4482; A. L. J. Beckwith, B. P. Hong and G. M. Williams, *J. Chem. Soc., Chem. Commun.*, 1989, 1202.
10 M. Tada and R. Shino, *J. Inorg. Biochem.*, 1991, **44**, 89.
11 J. Halpern, *Acc. Chem. Res.*, 1982, **15**, 238; J. A. M. Simmons and J. L. Beauchamp, *Chem. Rev.*, 1990, **90**, 629.
12 C. A. Tolman, *J. Am. Chem. Soc.*, 1970, **92**, 2956; *Chem. Rev.*, 1977, **77**, 313; W. C. Trogler and L. G. Marzilli, *Inorg. Chem.*, 1975, **14**, 2942; T. T. N. Flora, G. L. Rampel and J. Halpern, *Inorg. Chim. Acta*, 1983, **77**, 2167.
13 H. C. Brown and X. R. Minh, *J. Am. Chem. Soc.*, 1955, **77**, 1723; S. Mason, *J. Am. Chem. Soc.*, 1954, **76**, 1247.
14 (*a*) G. L. Geoffroy and M. S. Wrighton, *Organometallic Photochemistry*, Academic Press, London, 1979, p. 319; (*b*) B. T. Golding, T. J. Kemp and H. H. Shena, *J. Chem. Res.*, 1981, (*S*) 34; (*M*) 334; (*c*) R. Finke, B. L. Smith, B. J. Meyer and A. A. Malinero, *Inorg. Chem.*, 1983, **22**, 3677; (*d*) D. N. R. Rao and M. C. R. Symons, *J. Chem. Soc., Faraday Trans.*, 1984, **80**, 432.
15 B. P. Martin and R. G. Finke, *J. Am. Chem. Soc.*, 1990, **112**, 2419; M. C. S. Garr and R. G. Finke, *J. Am. Chem. Soc.*, 1992, **114**, 10440. See also ref. 14*c*.
16 J. Halpern, *Science*, 1985, **227**, 869; K. Brown and H. B. Brooks, *Inorg. Chem.*, 1991, **30**, 3420.
17 S. Baba, Y. Ohgo and S. Takeuchi, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 3967; Y. Ohgo, H. Wada, C. Ohtera, M. Ikarashi, S. Baba and S. Takeuchi, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 2656.
18 C. Tavagnacco, G. Balducci, G. Costa, K. Taschler and W. von Philipsborn, *Helv. Chim. Acta*, 1990, **73**, 1469; S. Shi, L. M. Daniel and J. H. Espenson, *Inorg. Chem.*, 1991, **30**, 3407; S. Shi, A. Bakac and J. H. Espenson, *Inorg. Chem.*, 1991, **30**, 3410.
19 B. P. Brauchaud and Y. L. Choi, *Tetrahedron Lett.*, 1988, **29**, 6037; C. Lopez and S. Alvarez, *J. Organomet. Chem.*, 1991, **414**, 245.
20 G. N. Schrauzer and R. J. Windgassen, *J. Am. Chem. Soc.*, 1966, **88**, 3738.
21 R. C. Stewart and L. G. Marzilli, *J. Am. Chem. Soc.*, 1978, **100**, 816.
22 G. N. Schrauzer, *Inorg. Synth.*, 1968, **11**, 65.
23 W. C. Trogler, R. C. Stewart, L. A. Epps and L. G. Marzilli, *Inorg. Chem.*, 1974, **13**, 1564.
24 Reported by N. Bresciani-Pahor, L. Randaccio, P. G. Toscana, A. C. Sandercock and L. G. Marzilli (*J. Chem. Soc., Dalton Trans.*, 1982, 129), but neither synthetic procedure nor physical constants other than crystallographic data were recorded.
25 R. D. Schuletz and L. Ciporin, *J. Org. Chem.*, 1958, **23**, 206.
26 G. M. Whitesides and T. L. Newirth, *J. Org. Chem.*, 1975, **40**, 3448.
27 G. Moad, E. Rizzardo and D. H. Solomon, *Aust. J. Chem.*, 1983, **36**, 1573.

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