

EPR/ENDOR Detection of Stable Ti^{III} and Ti^{IV} Radical Products Generated by Single Electron Transfer from (PrⁱO)₃TiCH₃

Michael Moscherosch and Wolfgang Kaim*

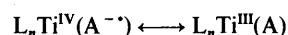
Institut für Anorganische Chemie, Universität Stuttgart, D-7000 Stuttgart 80, Germany

Single electron transfer reactions between the stereoselective carbanion source methyltriisopropoxytitanium(IV) as donor and α -diimines, ketones or α -dicarbonyls as π acceptor substrates exhibit a dichotomy with respect to the EPR-detectable paramagnetic 'escape' products. Substrates with very negative reduction potentials such as 2,2'-bipyridine yield Ti^{III} species, whereas more easily reducible molecules such as dinucleating 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine react to yield EPR-detectable Ti^{IV} complexes of the corresponding anion radicals. A very stable paramagnetic product has been isolated from the reaction between 3,5-di-*tert*-butyl-*o*-quinone (dtbq) and (PrⁱO)₃TiCH₃; this first thermally stable, but apparently configurationally labile, Ti^{IV} semiquinone complex [(dtbq⁻¹)Ti(OPrⁱ)₃][•] was studied by UV-VIS-NIR absorption and EPR/ENDOR spectroscopy.

Electron transfer reactions between organic π acceptor molecules and synthetically useful organometallic compounds have been studied with main group element species containing *e.g.* Li, Mg, Al, Si and Zn.¹⁻⁵ Some of these reactions, especially those with chelating substrates have proven to be of synthetic interest;²⁻⁴ thermal² and light-induced⁴ processes can yield different paramagnetic and diamagnetic products after metal-carbon bond cleavage, permitting the regioselective formation of recombination products.

The electron transfer nature of such reactions is evident from the occurrence of persistent paramagnetic 'escape' products, *i.e.* complexes between one-electron-reduced acceptor and an electrophilic metal species.¹⁻⁴ Scheme 1 illustrates the

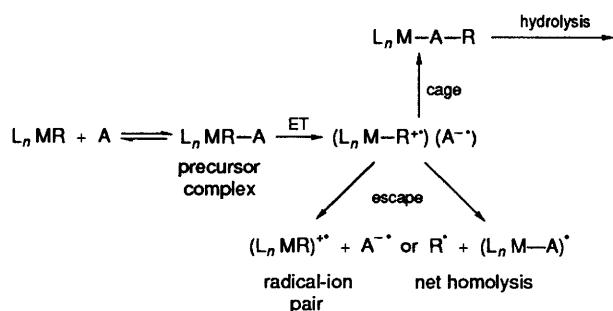
previous studies have demonstrated;¹⁵ both the substrate and the co-ligands on titanium should determine the contributions from either form in Scheme 2.



Scheme 2

The possible occurrence of low-valent titanium can create an additional type of reactivity towards acceptors; eventually, this could involve deoxygenation of carbonyl-containing substrates.¹⁶

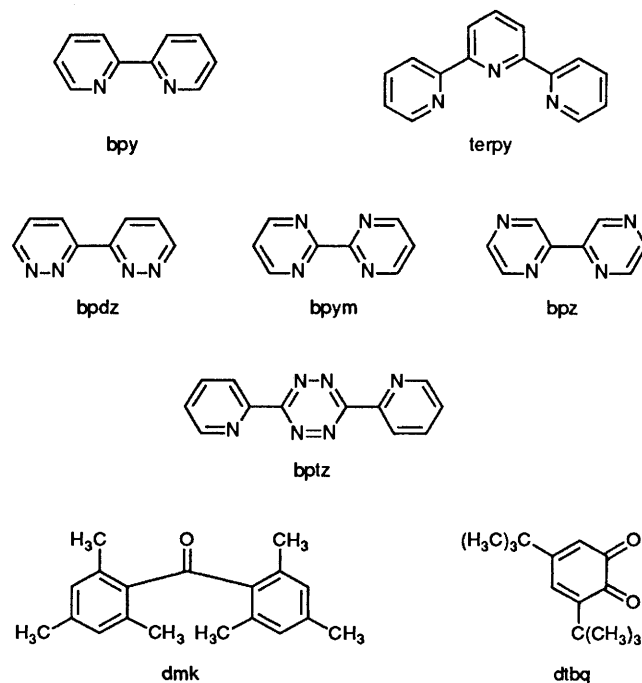
In this paper we describe the paramagnetic products observable by EPR/ENDOR spectroscopy in the reaction of (PrⁱO)₃TiCH₃ with π acceptor substrates of the carbonyl, α -dicarbonyl or α -diimine type. Included is the isolation of one particularly stable radical complex, the first isolable Ti^{IV} semiquinone compound; although complexes of nitroxides¹⁷ and ketyls¹⁸ with Ti(OR)_{*n*} were described, there has been only one previous report¹⁹ on labile photogenerated coordination compounds between the Ti^{IV} centre of (CpTiCl₂)⁺ and some effectively chelating^{1,5,20-22} *o*-semiquinone ligands.



Scheme 1 R = organometallic (C-bonded) ligand; A = acceptor; L_{*n*} = *n* co-ligands

mechanism leading to precursor complex, paramagnetic ('escape') and diamagnetic ('cage' or 'recombination') products.

In contrast to organometallic compounds of non-redox-active metals such as those mentioned above,¹ organotransition metal compounds offer the possible participation of metal *d* orbitals in the electron transfer process.⁶ Whereas organocobalt(III) complexes continue to be studied under electron transfer aspects in context with cobalamine chemistry,⁷ organotitanium compounds L_{*n*}TiR were primarily investigated with regard to their superior stereoselectivity.⁸⁻¹² The usefulness of organotitanium(IV) reagents such as (PrⁱO)₃TiCH₃ was attributed in part to conformational rigidity and chelate control in the transition state;⁸⁻¹² an electron transfer mechanism involving either substrate radical anions or Ti^{III} intermediates has not been considered for these reactions although other organotitanium species containing cyclopentadienyl groups were discussed under such aspects.^{13,14} The possibility of valence isomers (Scheme 2) is not unreasonable as



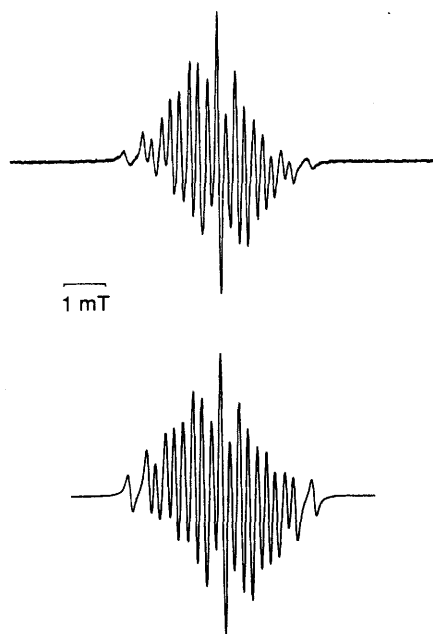


Fig. 1 Top: EPR spectrum of the persistent paramagnetic product from the reaction between bptz and $(\text{Pr}^{\text{O}})_3\text{TiCH}_3$ in THF solution at 295 K. Bottom: computer simulated spectrum with the data from Table 1 and a linewidth of 0.11 mT.

Table 1 EPR data^a of titanium-containing radical products from the reaction of acceptor ligands A with $(\text{Pr}^{\text{O}})_3\text{TiCH}_3$ in THF

A	$E_{\text{red}}(\text{A})^b$	g	$a(^{47,49}\text{Ti})$	$a(\text{X})$
dmk	-2.37 ^c	1.952	1.75 (200 K)	
bpy	-2.13	1.964	1.36	
terpy	-2.00	1.961	1.43 (250 K)	
bpdz	-1.72	2.0031	<0.5	
bpym	-1.73	2.0023	<0.5	
bpz	-1.59	2.0018	<0.5	
bptz ^d	-0.72	2.0039	0.098 ^e	0.443 ($2 \times ^{14}\text{N}$) 0.642 ($2 \times ^{14}\text{N}$) 0.326 ($1 \times ^1\text{H}$) ^f 0.066 ($1 \times ^1\text{H}$) 0.035 ($9 \times ^1\text{H}$) 0.005 ($9 \times ^1\text{H}$) ^g 0.522 ($3 \times ^{13}\text{C}$)
dtbq	-0.59	2.0043	0.064	0.247 ($1 \times ^1\text{H}$) ^h 0.072 ($1 \times ^1\text{H}$) 0.034 ($9 \times ^1\text{H}$) 0.275 ($1 \times ^1\text{H}$) ^b 0.072 ($1 \times ^1\text{H}$) 0.034 ($9 \times ^1\text{H}$)
		2.0043	ca. 0.06	
		2.0043		

^a Hyperfine coupling constants in mT. Measurements at 295 K except where noted. ^b Reduction potentials of free A in V vs. SCE. ^c Reference 29. ^d Dinuclear titanium radical complex. ^e $a(\text{Ti})/A_{\text{iso}}(\text{Ti}) = 0.098 \text{ mT}/17.75 \text{ mT} = 0.00552$. ^f Primary species; identical parameters in pentane. ^g From ENDOR measurements at 193 K. ^h Secondary species (see text); data from ENDOR measurements at 193 K.

Experimental

Materials.—The acceptor ligands were either commercially available or synthesized according to published procedures (bpdz,²³ bptz²⁴). Methyltriisopropoxytitanium(IV) was prepared, purified and used according to Reetz *et al.*²⁵ All manipulations were carried out under an atmosphere of dry argon.

Sample Preparation.—The acceptor substrate and freshly distilled $(\text{Pr}^{\text{O}})_3\text{TiCH}_3$ were dissolved separately in tetrahydro-

furan (THF), cooled to *ca.* 200 K and then mixed rapidly. A sample of this cold solution was transferred into a precooled (193 K) EPR tube.

Synthesis of $[(\text{dtbq}^{-1})\text{Ti}^{\text{IV}}(\text{OPr}^{\text{i}})_3]^{-}$.—Methyltriisopropoxytitanium (480 mg, 2 mmol) and 3,5-di-*tert*-butyl-*o*-benzoquinone (dtbq: 440 mg, 2 mmol) were each dissolved in pentane (10 cm³). The two solutions were mixed and stirred vigorously in a water-ice bath for 5 min, and the colour quickly turned from yellow to dark brown. After warming up and stirring for 1 h at ambient temperature the solution was evaporated to dryness. Recrystallization from toluene at 200 K yielded 568 mg (64%) of air- and moisture-sensitive brown crystals (Found: C, 61.75; H, 9.2; Ti, 11.7. $\text{C}_{23}\text{H}_{41}\text{O}_5\text{Ti}$ (445.47) requires C, 62.01; H, 9.28; Ti, 10.75%).

Instrumentation.—EPR and ENDOR spectra were recorded in the X band on a Bruker System ESP 300 equipped with an ENI A500 RF amplifier, a Bruker ER033 field frequency lock, a Bruker ER035M gaussmeter and a HP 5350B microwave counter. UV-VIS spectra were taken on a Shimadzu UV-160 spectrometer. Cyclic voltammetry was carried out in 1,2-dichloroethane-0.1 mol dm⁻³ Bu_4NClO_4 using three-electrode configuration (GCE, SCE, Pt) and a PAR 273/175 potentiostat and function generator.

Results

Dilute solutions of methyltriisopropoxytitanium(IV) in THF or pentane react rapidly with the π acceptor compounds to form paramagnetic species. In many instances, the reaction proceeds *via* intensely coloured intermediates which are short-lived (*ca.* 1 s) even at -80°C . While the composition of the resulting paramagnetic 'escape' species cannot be determined in every detail from EPR or ENDOR spectroscopy, there is an immediately obvious dichotomy concerning the g factor and the $^{47,49}\text{Ti}$ coupling (^{47}Ti : 7.75% natural abundance, $I = 5/2$, $A_{\text{iso}} = 17.75 \text{ mT}$; ^{49}Ti : 5.51% natural abundance, $I = 7/2$, $A_{\text{iso}} = 17.76 \text{ mT}$).

(i) Acceptors with reduction potentials $< -1.9 \text{ V vs. SCE}$ such as 2,2'-bipyridine (bpy), 2,2':6',2''-terpyridine (terpy) or dimesitylketone (dmk) yield typical²⁶ Ti^{III} signals with isotropic g factors of *ca.* 1.96 and titanium isotope couplings of *ca.* 1.5 mT (Table 1). The ketone, which has the most negative reduction potential in the series of substrates, forms a rather labile paramagnetic complex which exhibits the most pronounced metal character, *i.e.* the lowest g factor and the largest $a(^{47,49}\text{Ti})$ value.

(ii) Better π acceptors with reduction potentials $> -1.9 \text{ V vs. SCE}$ such as certain polyaza- α -diimines and the 3,5-di-*tert*-butyl-*o*-quinone yield EPR signals with $g > 2$ and, in some instances (Figs. 1 and 2), well-resolved and familiar^{20,21,27} hyperfine structure which indicates derivatives²² of the substrate radical anions (Table 1). Whereas the bidiazine²⁸ isomers 3,3'-bipyridazine (bpdz), 2,2'-bipyridimine (bpym) or 2,2'-bipyrazine (bpz) yield poorly resolved EPR spectra of radicals in low concentration, the dinucleating 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz) π acceptor ligand with its tetrazine-centred LUMO²⁷ forms a persistent radical with an easily analysed spectrum (Fig. 1, Table 1).

The sterically encumbered *o*-quinone dtbq reacts very rapidly with $(\text{Pr}^{\text{O}})_3\text{TiCH}_3$ to yield an isolable orange-brown paramagnetic solid. A dilute solution of this air-sensitive neutral species in pentane shows an EPR spectrum (Fig. 2) which can be computer simulated by assuming a rather small $^{47,49}\text{Ti}$ isotope coupling and a typical,^{5,20,21} ENDOR-supported dtbq semiquinone coupling pattern (Table 1).

In solution, this primary paramagnetic species undergoes time-dependent changes which can be conveniently monitored

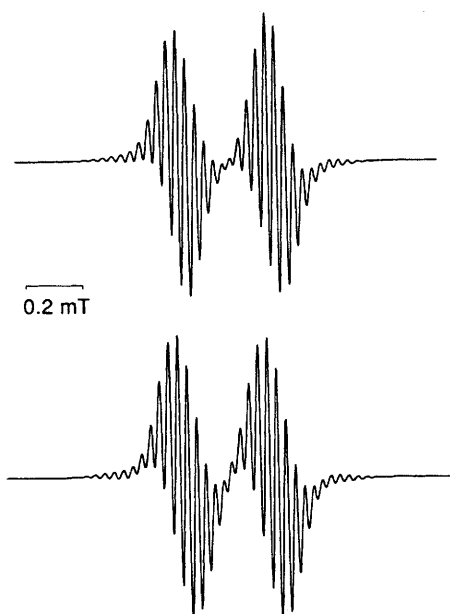


Fig. 2 Top: EPR spectrum of the isolated paramagnetic product from the reaction between dtbq and $(\text{Pr}^{\text{IV}}\text{O})_3\text{TiCH}_3$ in pentane solution at 295 K. Bottom: computer simulated spectrum with the data from Table 1 (including ^{13}C and $^{47,49}\text{Ti}$) and a linewidth of 0.019 mT.

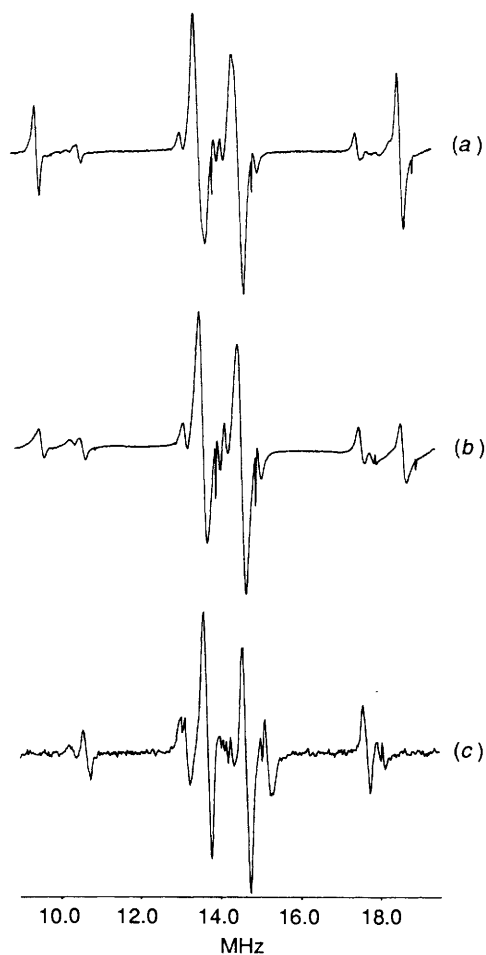


Fig. 3 ENDOR spectra (193 K) in pentane solution of the isolated paramagnetic product from the reaction between dtbq and $(\text{Pr}^{\text{IV}}\text{O})_3\text{TiCH}_3$. (a) Spectrum of freshly dissolved solid, (b) after 80 min, (c) after 300 min.

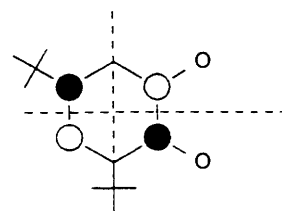


Fig. 4

by EPR and ENDOR. Thus, even the ENDOR spectra of freshly prepared solutions exhibit small additional resonances in the 4-H and *tert*-butyl coupling regions [Fig. 3(a)]. Some of these secondary signals increase irreversibly and virtually temperature-independently with time at the expense of the original features, more rapidly in THF solution than in pentane [Fig. 3(b),(c)].

Discussion

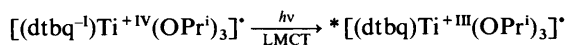
In analogy to SET reactions from other alkylmetal reagents^{2,4,30} we attribute the conspicuous colours of the short-lived intermediates from the radical-producing reactions between $(\text{Pr}^{\text{IV}}\text{O})_3\text{TiCH}_3$ and the substrates to the ligand-to-ligand charge transfer transitions of precursor complexes (Scheme 1).

In the case of poor acceptors ($E_{\text{red}} < -1.9$ V vs. SCE) it is evident that the reduction equivalents created *via* SET processes (Scheme 1) are used to reduce not the (metal-bound) acceptor but the Ti^{IV} metal centre which is coordinated to a reduced or methylated ligand. In contrast, better π acceptors ($E_{\text{red}} > -1.9$ V) yield ligand-centred paramagnetic species, *i.e.* radical anion ligands²² coordinated to Ti^{IV} . This is evident from $g > 2$ and from well resolved and familiar^{20,21,27} hyperfine coupling in some instances (Figs. 1 and 2). The spectrum of the persistent radical product formed from the dinucleating π acceptor ligand bptz with its tetrazine-centred LUMO²⁷ shows coupling from two different pairs of ^{14}N nuclei which are attributed to the coordinating (0.642 mT) and non-coordinating nitrogen atoms (0.443 mT) of the tetrazine ring in a symmetrical dinuclear complex $\{(\text{bptz}^-)[\text{Ti}^{\text{IV}}(\text{OPr}^{\text{I}})_n]_2\}^{(7-2n)+}$. The splitting of tetrazine N coupling constants, the g factor and the $^{47,49}\text{Ti}$ isotope coupling as determined at the margins of the spectrum (Fig. 1 and Table 1) are quite similar to the values obtained for the Cr^0 complex $\{(\text{bptz}^-)[\text{Cr}(\text{CO})_4]_2\}^-$: $a_{\text{N}} = 0.459$ and 0.622 mT, $g = 2.033$, $a(^{53}\text{Cr}) = 0.11$ mT, $a(\text{M})/A_{\text{iso}}(\text{M}) = 0.00488$.²⁷

The EPR spectrum of the primary isolable radical product from the reaction of $(\text{Pr}^{\text{IV}}\text{O})_3\text{TiCH}_3$ with dtbq could be simulated by assuming a rather small $^{47,49}\text{Ti}$ isotope coupling and a typical,^{5,20,21} ENDOR-supported dtbq semiquinone coupling pattern (Table 1). Occupation of a $\pi(\text{as})$ type MO (Fig. 4) leads to a large coupling for 4-H (*ca.* 0.3 mT) and a relatively large hyperfine splitting from the protons of the *tert*-butyl group in position 5 (*ca.* 0.03 mT); the ring proton in position 6 (*ca.* 0.07 mT) and the other *tert*-butyl group lie in a π nodal plane (Fig. 4) and thus have rather small proton coupling constants.

While the EPR hyperfine values for a $(\text{dtbq}^-)/\text{Ti}^{\text{IV}}$ complex are not unexpected,^{5,19,21} the time-dependent EPR/ENDOR changes (Fig. 3) clearly indicate a configurational lability which would be typical¹⁹ for a neutral pentacoordinated species $[(\text{dtbq})\text{Ti}(\text{OPr}^{\text{I}})_3]$ as suggested by elemental analysis. We can only speculate at this point that these changes could be due to slow configurational changes in a trigonal-bipyramidal situation (pseudorotation) or to a change in coordination number at the metal; both an increase in coordination number to 6, through addition of another ligand, or a decrease to 4,¹⁹ perhaps through reduced hapticity of the bulky, unsymmetrical *o*-semiquinone ligand are conceivable.

The solution of the radical $[(dtbq^{-1})Ti^{+IV}(OPr^i)_3]^{\cdot}$ in pentane exhibits two intense VIS-NIR absorptions with maxima at 489 and 794 nm. The latter indicates an allowed transition at rather low energy which we attribute to a ligand-to-metal charge transfer (LMCT).



Excitation by a photon would thus induce intramolecularly the same change of oxidation states which is caused in the ground state by the variation of the reduction potential of the acceptor (Table 1). Since semiquinones can serve both as acceptors and donors, they may thus engage in MLCT transitions from electron rich Ru^{II} or, as shown here, in LMCT transitions towards maximally oxidized metal centres such as Ti^{IV} .

Summarizing, we have shown that the 'Grignard analogue' $(Pr^iO)_3TiCH_3$ does undergo single electron transfer reactions with carbonyl, α -dicarbonyl and α -diimine substrates and that the paramagnetic products can be formed as Ti^{III} or as Ti^{IV} /radical species, depending on the reduction potential of the acceptor. A remarkably persistent Ti^{IV}/o -semiquinone complex which exhibits a low-energy LMCT transition and a time-dependent ENDOR spectrum upon dissolution could be isolated as an unusually^{1,2} high yield escape product. Diamagnetic products will have to be characterized in order to obtain a more comprehensive picture within the overall mechanistic scheme (Scheme 1).

Acknowledgements

This work was supported by Volkswagenstiftung (program 'Organometallics for Organic Synthesis'), Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie.

References

- W. Kaim, *Acc. Chem. Res.*, 1985, **18**, 160.
- G. van Koten, in *Organometallics in Organic Synthesis*, eds. A. deMeijere and H. tom Dieck, Springer, Berlin, 1987, p. 277.
- W. Kaim and B. Olbrich-Deussner, in *Organometallic Radical Processes*, ed. W. C. Trogler, Elsevier, Amsterdam, 1990, p. 173.
- M. Kaupp, H. Stoll, H. Preuss, W. Kaim, T. Stahl, G. van Koten, E. Wissing, W. J. J. Smeets and A. L. Spek, *J. Am. Chem. Soc.*, 1991, **113**, 5606.
- A. V. Lobanov, G. A. Abakumov and G. A. Razuvaev, *Dokl. Akad. Nauk SSSR*, 1977, **235**, 824; G. A. Razuvaev, G. A. Abakumov, E. S. Klimov, E. N. Gladyshev and P. Y. Bayushkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, 1128.
- J. P. Collmann, L. S. Hegedus, J. R. Norton and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, 1987.
- B. Branchaud and G.-X. Yu, *Organometallics*, 1991, **10**, 3795.
- M. T. Reetz, *Organotitanium Reagents in Organic Synthesis*, Springer, Berlin, 1986.
- M. T. Reetz, *Angew. Chem.*, 1984, **96**, 542; *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 556.
- B. Weidmann and D. Seebach, *Angew. Chem.*, 1983, **95**, 12; *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 31.
- M. T. Reetz, *Pure Appl. Chem.*, 1988, **60**, 1607.
- M. T. Reetz, *Angew. Chem.*, 1991, **103**, 1559; *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1531.
- M. J. Burk, W. Tumas, M. D. Ward and D. R. Wheeler, *J. Am. Chem. Soc.*, 1990, **112**, 6133.
- T. V. RajanBabu, W. A. Nugent and M. S. Beattie, *J. Am. Chem. Soc.*, 1990, **112**, 6408.
- A. M. McPherson, B. F. Fieselmann, D. L. Lichtenberger, G. L. McPherson and G. D. Stucky, *J. Am. Chem. Soc.*, 1979, **101**, 3425.
- J. E. McMurry, *Chem. Rev.*, 1989, **89**, 1513.
- A. H. Cohen and B. M. Hoffman, *Inorg. Chem.*, 1974, **13**, 1484.
- K. J. Covert, P. T. Wolczanski, S. A. Hill and P. J. Krusic, *Inorg. Chem.*, 1992, **31**, 66.
- A. Vlcek, Jr., *J. Organomet. Chem.*, 1985, **297**, 43.
- J. A. Pedersen, *Handbook of EPR Spectra from Quinones and Quinols*, CRC Press, Boca Raton, 1985.
- A. von Zelewsky, C. Daul and C. W. Schlöpfer, *Landolt-Börnstein, Physical and Chemical Tables*, Springer, Berlin, 1987; New Series, Vol. II/17a, p. 199.
- C. G. Pierpont and R. M. Buchanan, *Coord. Chem. Rev.*, 1981, **38**, 45; W. Kaim, *Coord. Chem. Rev.*, 1987, **76**, 187.
- J. J. Lafferty and F. H. Case, *J. Org. Chem.*, 1987, **32**, 1591.
- F. Dallacker, *Monatsh. Chem.*, 1960, **91**, 294.
- M. T. Reetz, J. Westermann, R. Steinbach, B. Wenderoth, R. Peter, R. Ostarek and S. Maus, *Chem. Ber.*, 1985, **118**, 1421.
- B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 136.
- S. Kohlmann, V. Kasack, E. Roth and W. Kaim, *J. Chem. Soc., Faraday Trans.*, 1989, **85**, 4047.
- W. Kaim and S. Ernst, *J. Phys. Chem.*, 1986, **90**, 5010.
- M. Svaan and V. D. Parker, *Acta Chem. Scand. Ser. B*, 1982, **36**, 365.
- J. Baumgarten, C. Bessenbacher, W. Kaim and T. Stahl, *J. Am. Chem. Soc.*, 1989, **111**, 2126 and 5017.
- M. Haga, E. S. Dodsworth and A. B. P. Lever, *Inorg. Chem.*, 1986, **25**, 447.

Paper 2/01834I

Received 30th March 1992

Accepted 12th May 1992