

Journal of Organometallic Chemistry, 440 (1992) 145–152
Elsevier Sequoia S.A., Lausanne
JOM 22919

Electron transfer catalyzed substitution in carbonyl complexes

VI*. Highly variable rates of substitution by tetracyanoethylene

Brigitte Schwederski, Wolfgang Kaim, Barbara Olbrich-Deussner
and Thomas Roth

*Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55,
W-7000 Stuttgart 80 (Germany)*

(Received April 24, 1992)

Abstract

Rates of substitution of tetrahydrofuran (THF) or trimethyl phosphite by tetracyanoethylene (TCNE) in organometallic complexes (THF)W(CO)₅, (THF)Cr(CO)₅, [P(OMe)₃]Cr(CO)₂(C₆Me₆), (THF)Mn(CO)₂(C₅Me₅) and (THF)Mn(CO)₂(C₅H₄Me) in THF solution, have been determined. As indicated by the calculated second-order rate constants *k*, the manganese complexes (*k* > 1900 M⁻¹ s⁻¹) react by a factor of at least 10⁴ more rapidly than the W(CO)₅ complex (*k* = 0.043 M⁻¹ s⁻¹). Measurements of recombination kinetics of photodissociated (acpy)Mn(CO)₂(C₅Me₅) (acpy = 4-acetylpyridine) in THF show that the substitution by TCNE of THF in the corresponding solvent complex proceeds faster by a factor of 2 × 10⁴. Of the two chromium complexes, the pentacarbonyl/THF system has a value of *k* of 0.39 M⁻¹ s⁻¹ whereas the phosphite ligand in [P(OMe)₃]Cr(CO)₂(C₆Me₆) is substituted by TCNE with *k* = 1.59 M⁻¹ s⁻¹. The results and their correlation with electrochemical data support a self-induced homogeneous electron transfer mechanism: it is proposed that electron transfer between the reaction partners TCNE and the organometallic precursor leads to substitutionally-labile 17 valence electron complexes as essential intermediates in the catalytic chain. Efficient oxidation of the precursors by the TCNE-substituted 17 VE species is possible because of intramolecular metal-to-TCNE electron transfer, especially in the σ -coordinated products with mixed carbonyl/carbocycle ligands.

Introduction

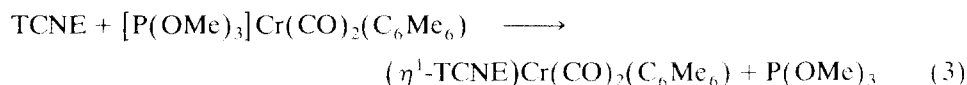
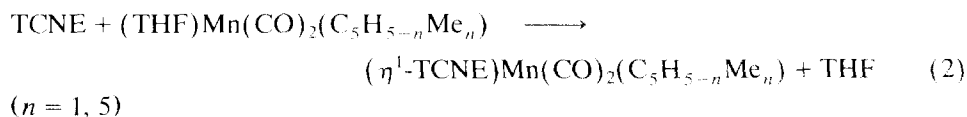
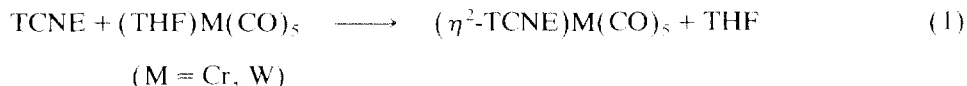
Reactions of electron-rich organometallic compounds with acceptor substrates are often characterized by free radical mechanisms [2–4], involving single electron transfer steps [5–7]. A continuing challenge in this area is to relate observed rates

Correspondence to: Dr. W. Kaim.

* For Part V, see ref. 1.

to mechanisms and to energy data for the precursors, particularly with redox potentials in the case of electron transfer [2-7].

A small but extremely effective π -acceptor is tetracyanoethylene (TCNE), which readily reacts with many organometallics, yielding a variety of unusual complexes [8-15]. We have previously reported qualitative observations revealing apparently very different rates of substitution of tetrahydrofuran (THF) ligands in photogenerated solvent complexes such as in eqns. 1 or 2 by TCNE [1]; a similar reaction involving the substitution of trimethylphosphite in eq. 3 by TCNE was also observed to proceed rather rapidly [1,15].

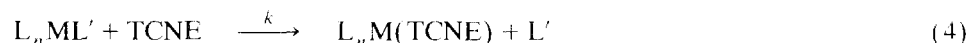


In this paper we present kinetic data on the five substitution reactions 1-3, which yield complexes with η^1 (N)- or η^2 (C=C)-coordinated TCNE⁽⁻⁾ [1]. Specifically, an attempt is made to relate the considerable differences in rates to the redox potentials of precursors and products within a self-induced electron transfer catalytic mechanism [16], which we describe as electron-transfer autocatalysis.

Results and discussion

When the TCNE complexes (TCNE)M(CO)₅, M = Cr, W, and (TCNE)Mn(CO)₂(C₅H_{5-n}Me_n), n = 1 and 5, were prepared [1] from the THF solvates by reactions (1) and (2), a marked difference in the rates of their formation was noted. A quantitative determination of these differences was therefore desirable.

Reactions (1-3) all showed simple pseudo-first order kinetics when the organometallic precursor was treated with at least a ten-fold molar excess of TCNE. Such behaviour is expected for a straightforward substitution as depicted in eq. 4.



Depending on the very characteristic [1] charge transfer absorption maxima of the TCNE complexes formed, various monitoring wavelengths in the visible spectrum were chosen for the kinetic measurements (Table 1, Fig. 1).

Because of the wide range of rates of the substitutions (Table 2) the mixed carbonyl/carbocycle containing systems (2) and (3) had to be studied *via* stopped-flow techniques. Even so, the rate of substitution of THF in (THF)Mn(CO)₂(C₅H₄Me) by TCNE was too high to measure under the conditions used, the reaction being complete within the dead-time of the stopped-flow instrument used (*ca.* 4 ms). From that observation a lower limit for the second-order rate constant of 14000 M⁻¹ s⁻¹ can be estimated.

Table 1

Absorption maxima of TCNE complexes in THF

complex	λ_{\max} , nm
(CO) ₅ W(TCNE)	677
(CO) ₅ Cr(TCNE)	741
(C ₆ Me ₆)X(CO) ₂ Cr(TCNE)	661
	463
(C ₅ Me ₅)X(CO) ₂ Mn(TCNE)	753
	392
(C ₅ H ₄ Me)X(CO) ₂ Mn(TCNE)	785

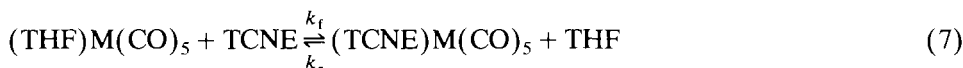
All other reactions were pseudo-first order in $[L_nML']$ for at least four half-lives and conformed to the rate expression:

$$d[L_nM(TCNE)]/dt = k_{\text{obs}}[L_nML'] \quad (5)$$

$$k_{\text{obs}} = k[TCNE] \quad (6)$$

The second-order rate constants k calculated from eq. 6 (Fig. 2) show a spread of almost 5 orders of magnitude (Table 3).

Of the reactions investigated, only the two slowest, which involve the pentacarbonylmetals, showed a statistically non-zero intercept in the plots of k_{obs} vs. $[TCNE]$, indicating the existence of an equilibrium (7).



(M = Cr, W)

The existence of this equilibrium is also evident from a change of the absorbance at infinite time, A_∞ , owing to changes in the amount of the TCNE complex formed, this amount depending on the excess of TCNE used. The equilibrium constants (8) for the reactions (7) were calculated as $140 \pm 40 \text{ M}^{-1}$ for M = W and $340 \pm 40 \text{ M}^{-1}$ for M = Cr.

$$K = [(TCNE)M(CO)_5] / [(THF)M(CO)_5][TCNE] = k_f/k_r \quad (8)$$

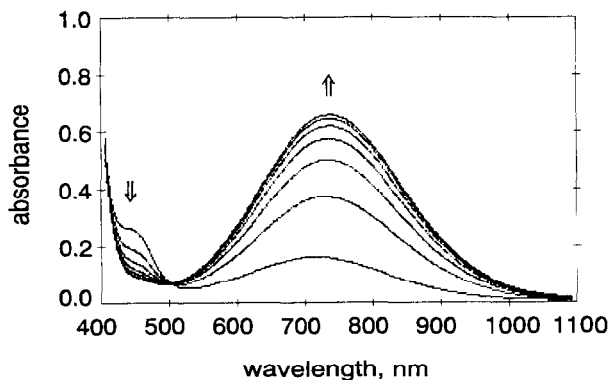


Fig. 1. Absorption spectra for the reaction of $(THF)Cr(CO)_5$ with TCNE in THF. Spectra were recorded at intervals of 120 s, starting at $t = 120$ s.

Table 2

Kinetic data for the substitution of THF or trimethylphosphite by TCNE in THF solution

complex	$10^3 \times [\text{TCNE}], M$	$10^3 \times k_{\text{obs}}, s^{-1}$
$(\text{CO})_5\text{W}(\text{THF})^a$	5.20	0.475
	10.4	0.713
	15.6	1.12
	20.8	1.16
	26.0	1.36
$(\text{CO})_5\text{Cr}(\text{THF})^b$	1.29	1.68
	1.55	1.48
	2.70	2.41
	3.86	2.62
	5.41	3.77
	6.18	3.88
	7.73	4.29
	9.37	4.35
18.7	8.60	
$(\text{C}_6\text{Me}_6)(\text{CO})_2\text{Cr}[\text{P}(\text{OMe})_3]^c$	2.57	3.99
	5.14	6.93
	16.5	28.9
	24.7	43.0
	33.0	55.6
	49.5	74.4
$(\text{C}_5\text{Me}_5)(\text{CO})_2\text{Mn}(\text{THF})^d$	2.80	4500
	3.70	7200
	4.60	9000

^a $[(\text{CO})_5\text{W}(\text{THF})] = 1.7 \times 10^{-4} M$; $\lambda = 680 \text{ nm}$; $T = 20^\circ\text{C}$; Perkin-Elmer 554. ^b $[(\text{CO})_5\text{Cr}(\text{THF})] = 6.7 \times 10^{-5} M$; $\lambda = 740 \text{ nm}$; $T = 20^\circ\text{C}$; Shimadzu UV-160. ^c $[(\text{C}_6\text{Me}_6)(\text{CO})_2\text{Cr}[\text{P}(\text{OMe})_3]] = 4.9 \times 10^{-4} M$; $\lambda = 700 \text{ nm}$; $T = 20^\circ\text{C}$; Durrum stopped-flow. ^d $[(\text{C}_5\text{Me}_5)(\text{CO})_2\text{Mn}(\text{THF})] = 2.0 \times 10^{-4} M$; $\lambda = 720 \text{ nm}$; $T = 20^\circ\text{C}$; Durrum stopped-flow.

Since TCNE is a well-established one-electron oxidant towards organometallic compounds [1,2,4,9,11,17], we have based the mechanistic interpretation of the highly variable rates of substitution by TCNE on electrochemical data. Whereas the products of substitution by TCNE exhibit reversible reduction behaviour, the organometallic precursors (solvates) undergo irreversible oxidation to labile [18,19] 17 valence electron (VE) species. Anodic peak potentials of the donors and half-wave reduction potentials of the TCNE acceptor and the product complexes are summarized, together with the second order rate constants, in Table 3.

The potentials can be correlated with the rates in Table 3 in terms of the mechanism depicted in Scheme 1.

The relation between the E_{red} of TCNE and the anodic peak potentials of some of the organometallic precursors L^*ML_n , especially the carbocycle-containing species, suggests the possibility of an initial homogeneous electron transfer, leading to a free TCNE anion radical and substitutionally labilized 17 VE cations $[L^*ML_n]^+$. While the irreversibility of the oxidation of L^*ML_n and the lack of information on the inner- or outer-sphere mechanism of this start reaction prevents us from determining the exact degree of electron exchange, the trend within

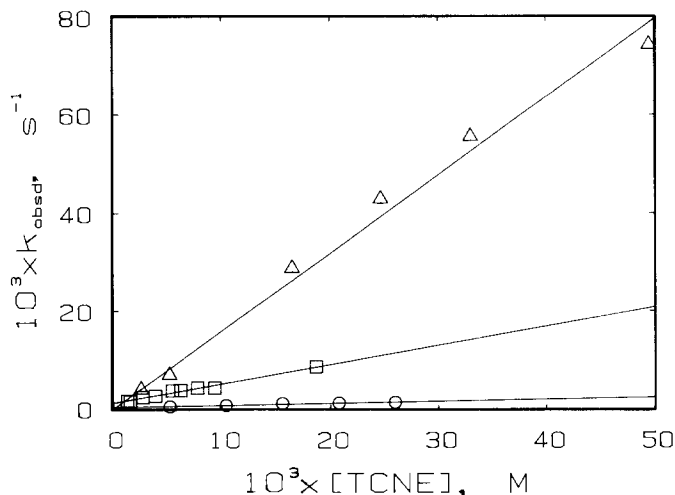


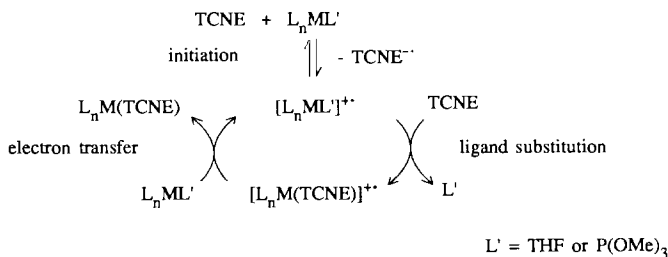
Fig. 2. Dependence of k_{obs} on the TCNE concentration [TCNE] for the reactions of $(\text{THF})\text{M}(\text{CO})_5$, $\text{M} = \text{Cr}$ (\square) or W (\circ) and of $[\text{P}(\text{OMe})_3]\text{Cr}(\text{CO})_2(\text{C}_6\text{Me}_6)$ (Δ) with TCNE in THF solution. The lines represent a least-squares fit to the experimental data.

Table 3

Electrochemical potentials E (V vs. Fc/Fc^+)^a and second-order rate constants k ($\text{M}^{-1} \text{s}^{-1}$) relevant to the substitution $\text{L}'\text{ML}_n + \text{TCNE} \rightarrow (\text{TCNE})\text{ML}_n + \text{L}'$ in THF solution^b

ML_n	L'	$E_{\text{ox}}(\text{L}'\text{ML}_n)^c$	$(\text{TCNE})\text{ML}_n^d$		k^e
			E_{ox}	E_{red}	
$\text{W}(\text{CO})_5$	THF	+0.48	+0.91	-0.14	0.043
$\text{Cr}(\text{CO})_5$	THF	+0.20	+0.73	-0.20	0.39
$\text{Mn}(\text{CO})_2(\text{C}_5\text{H}_4\text{Me})$	THF	+0.08	^e	^e	> 14000 ^f
$\text{Mn}(\text{CO})_2(\text{C}_5\text{Me}_5)$	THF	-0.22	+0.50	-0.60	1900
$\text{Cr}(\text{CO})_2(\text{C}_6\text{Me}_6)$	$\text{P}(\text{OMe})_3$	-0.22	+0.38	-0.91	1.59

^a E_{ox} : Anodic peak potentials for irreversible oxidation; E_{red} : Half-wave potentials for reversible reduction. ^b TCNE has $E_{\text{red}} = -0.22$ V vs. Fc/Fc^+ in acetonitrile/0.1 M Bu_4NClO_4 . ^c In THF/0.1 M Bu_4NClO_4 ; scan rate 200 mV/s. ^d In acetonitrile/0.1 M Bu_4NClO_4 ; scan rate 100 mV/s (ref. 1, Fc/Fc^+ has +0.46 V vs. SCE under the conditions applied). ^e Not determined. ^f Lower limit from dead-time of stopped-flow instrument.



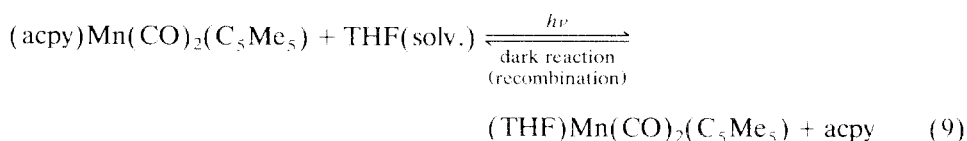
Overall stoichiometry: $\text{L}'_n\text{ML}' + \text{TCNE} \longrightarrow \text{L}'_n\text{M}(\text{TCNE}) + \text{L}'$

Scheme 1. Self-induced electron transfer catalytic mechanism for the substitution of L' by TCNE.

the series of Table 3 clearly points to an increase in the extent of formation of potentially chain-carrying [18] 17 VE species on lowering of $E_{\text{ox}}(L'ML_n)$.

Substitution of $L' = \text{THF}$ or $\text{P}(\text{OMe})_3$ by TCNE leads to still cationic 17 VE complexes which can, however, close the electron transfer catalytic cycle (Scheme 1) by oxidizing the precursor complexes. This second requirement for a self-induced electron transfer catalytic reaction is fulfilled because the TCNE product complexes have generally higher peak potentials for anodic oxidation than the THF solvates or the phosphite complex in the case of $\text{Cr}(\text{CO})_2(\text{C}_6\text{Me}_6)$ (Table 3). The high oxidation peak potentials of the products are a consequence of the very low basicity of TCNE; alternatively, they may be attributed to the partial or even complete intramolecular electron transfer from the metal to the TCNE ligand. The approximate formulation $(\text{TCNE}^-)(^+ML_n)$ illustrates why such species may be difficult to oxidize; the (reversible) reduction of most product complexes at potentials more negative than E_{red} of TCNE lends further support to this idea (Table 3).

Rapid initial electron transfer (if favourable) between the reaction partners, facile substitution of the first chain carrier, and efficient homogeneous electron exchange between oxidized product and precursor can lead to fast substitution as indicated in Table 3. There is an approximate correlation between the ease of oxidation of the precursor and the rate of substitution: the pentacarbonyl tungsten system shows essentially no effect of special acceleration whereas the manganese compounds react extraordinarily rapidly. With "normal" two electron donors such as acetonitrile [19] or the heterocycles 4-acetylpyridine (acpy) or pyrazine [20] the exchange of THF in complexes $(\text{THF})\text{Mn}(\text{CO})_2(\text{C}_5\text{R}_5)$ is rather sluggish despite the presence of low-lying magnetically and ligand-field-excited states; this slow substitution has even been held to be responsible for the failure [21] to obtain dinuclear complexes of pyrazine [20]. In the course of studies directed at the known [22] and recently rationalized [23] photolability of certain complexes $(\text{L})\text{Mn}(\text{CO})_2(\text{C}_5\text{R}_5)$ we have also measured (Table 4) and calculated the rate of recombination applicable to eq. 9.



(acpy: 4-acetylpyridine ($E_{\text{red}} = -2.07 \text{ V vs. Fc/Fc}^+$))

Table 4

Kinetic data for the substitution reaction THF/4-acetylpyridine (acpy) in photogenerated $(\text{THF})\text{Mn}(\text{CO})_2(\text{C}_5\text{Me}_5)^a$

$10^2 \times [\text{acpy}], M$	$10^3 \times k_{\text{obs}}, \text{s}^{-1}{}^b$
1.65	1.56
3.32	3.30
4.43	4.15
6.65	6.47

^a Recombination reaction of light-induced dissociation in THF solution (eq. 9). ^b Monitored at absorption maximum of 512 nm.

The calculated second-order rate constant of $0.096 \text{ M}^{-1} \text{ s}^{-1}$ for the substitution of THF by 4-acpy (eq. 9) is smaller by more than 4 orders of magnitude than the corresponding rate for TCNE (Table 3), confirming the operation of a special mechanism for the reaction of the latter.

While the effect of the ease of oxidation of the precursor complex in the start reaction can be semi-quantitatively assessed from peak potentials, the variations of the substitution process proper [24] within the catalytic cycle (Fig. 3) can only be interpreted qualitatively. It is obvious, however, that the sterically more hindered pentamethylcyclopentadienylmanganese complex reacts more slowly than the monomethylcyclopentadienyl analogue despite a slightly lower oxidation potential. Similarly, the substitution of trimethylphosphite should be much more difficult than that of THF, yet even the P(OMe)_3 complex of the very electron-rich $\text{Cr(CO)}_2(\text{C}_6\text{Me}_6)$ undergoes the exchange with TCNE fairly rapidly (Table 3). The THF solvate of $\text{Cr(CO)}_2(\text{C}_6\text{Me}_6)$ is too labile to serve as a well-defined precursor.

The catalysis scheme in Fig. 3 draws attention to a mechanism by which unusually fast exchange reactions can proceed *via* "hidden" electron transfer steps; such self-induced or autocatalytic electron transfer processes require no initiation from external electron sources or acceptors such as chemical oxidants or reductants, electrodes, or light [6,18,19]. Processes of the type shown in Fig. 3 may thus be part of efficient cycles in homogeneous organometallic catalysis; in any case, they are most certainly responsible for other "anomalously" facile substitution reactions involving TCNE [9,25].

Experimental

Reagents

The THF used in the kinetic measurements was dried by reflux over potassium under argon. The precursor complexes were prepared by published procedures [1,15,16,23]; in the case of THF solvates this was by prolonged photolysis of dilute solutions (about 0.001 M) of M(CO)_6 , $\text{M} = \text{Cr, W, or } (\text{C}_5\text{R}_5)\text{(CO)}_3\text{Mn}$ at -35°C . The typical extent of conversion was $> 90\%$ as indicated by IR spectroscopy.

Instrumentation and measurements

Electrochemical potentials of the TCNE complexes were obtained by cyclic voltammetry in acetonitrile/ $0.1 \text{ M Bu}_4\text{NClO}_4$ [1], and the solvent complexes were studied in THF/ $0.1 \text{ M Bu}_4\text{NClO}_4$. A PAR 273 potentiostat was used in conjunction with a three electrode configuration: glassy carbon working electrode, platinum counter electrode, SCE or Ag/AgCl as reference. Potentials were determined with the ferrocene/ferricinium couple as internal reference; the standard scan rate was 100 mV/s for the TCNE complexes and 200 mV/s for the solvates.

For kinetic measurements, the solutions of the THF complexes were diluted to *ca.* 0.1 mM . Concentrations were estimated from the concentrations of the precursor complexes, assuming $> 90\%$ efficiency of photolysis. Under all conditions, the metal complexes were the limiting reagents ($[\text{L}_n\text{ML}'] \ll [\text{TCNE}]$, pseudo-first order) and their exact concentrations were irrelevant for the determination of the rate constants. Tests of the precursor complexes revealed no interfering reactions under the conditions and on the time scale used. Solutions of $[\text{P(OMe)}_3]\text{Cr(CO)}_2(\text{C}_6\text{Me}_6)$ and TCNE in THF were prepared by weight. The

recombination reaction (9) was studied by irradiating a 3×10^{-4} M solution of (acpy)Mn(CO)₂(C₅R₅) [23] in THF in the presence of various amounts of acpy for 10 s with a 50 W HBO lamp. Recombination of the THF solvate with acpy was monitored using the MLCT band at 512 nm.

A Shimadzu UV/Vis spectrometer UV-160, a Perkin Elmer spectrophotometer 554 and a Durrum stopped-flow spectrophotometer with 4 ms dead time [26], interfaced to a Zenith PC, were used to study the reaction kinetics at the wavelengths indicated in Table 1.

Acknowledgments

This work was supported by grants from Volkswagenstiftung and Deutsche Forschungsgemeinschaft. We thank Professor H. Elias, TH Darmstadt (Germany) and Professor D.W. Margerum, Purdue University (USA), for access to instruments in their research groups for part of this work.

References

- 1 B. Olbrich-Deussner, W. Kaim and R. Gross-Lannert, *Inorg. Chem.*, 28 (1989) 3113.
- 2 J.K. Kochi, *Organometallic Mechanisms and Catalysis*, Academic Press, London, 1978.
- 3 M. Chanon (Ed.), *Importance of Paramagnetic Organometallic Species in Activation, Selectivity and Catalysis*, Kluwer Academic Publishers, Dordrecht, 1989.
- 4 W.C. Troglor (Ed.), *Organometallic Radical Processes*, Elsevier, Amsterdam, 1990.
- 5 W. Kaim, in A. Müller, E. Diemann, W. Junge and H. Ratajczak (Eds.) *Electron and Proton Transfer in Chemistry and Biology*, Elsevier, Amsterdam, 1992, p. 45.
- 6 M. Chanon and M.L. Tobc, *Angew. Chem.*, 94 (1982) 27; *Angew. Chem., Int. Ed. Engl.*, 21 (1982) 1.
- 7 D. Astruc, *Angew. Chem.*, 100 (1988) 662; *Angew. Chem., Int. Ed. Engl.*, 27 (1988) 643.
- 8 W.H. Baddley, *Inorg. Chim. Acta Rev.*, 2 (1968) 7.
- 9 M.F. Rettig and R.M. Wing, *Inorg. Chem.*, 8 (1969) 2685.
- 10 W. Beck, R. Schlodder and K.H. Lechler, *J. Organomet. Chem.*, 54 (1973) 503.
- 11 J.S. Miller, A.J. Epstein and W.M. Reiff, *Acc. Chem. Res.*, 21 (1988) 114.
- 12 R. Gross-Lannert, W. Kaim and B. Olbrich-Deussner, *Inorg. Chem.*, 29 (1990) 5046.
- 13 J.M. Manriquez, G.T. Yee, R.S. Mel'ean, A.J. Epstein and J.S. Miller, *Science*, 252 (1991) 1415.
- 14 S.E. Bell, J.S. Field, R.J. Haines, M. Moscherosch, W. Matheis and W. Kaim, *Inorg. Chem.*, 31 (1992) 3269.
- 15 K.L. Amos and N.G. Connelly, *J. Organomet. Chem.*, 194 (1980) C57.
- 16 W. Kaim, B. Olbrich-Deussner, R. Gross, S. Ernst, S. Kohlmann and C. Bessenbacher, in ref. 3, p. 283.
- 17 J. Baumgarten, C. Bessenbacher, W. Kaim and T. Stahl, *J. Am. Chem. Soc.*, 111 (1989) 2126 and 5017.
- 18 J.W. Hershlberger, R.J. Klingler and J.K. Kochi, *J. Am. Chem. Soc.*, 105 (1983) 61.
- 19 P.M. Zizelman, C. Amatore and J.K. Kochi, *J. Am. Chem. Soc.*, 106 (1984) 3771.
- 20 R. Gross and W. Kaim, *Inorg. Chem.*, 25 (1986) 498.
- 21 P.L. Gaus, N. Marchant, M.A. Marsinek and M.O. Funk, *Inorg. Chem.*, 23 (1984) 3269.
- 22 P.J. Giordano and M.S. Wrighton, *Inorg. Chem.*, 16 (1977) 160.
- 23 W. Kaim, T. Roth, B. Olbrich-Deussner, R. Gross-Lannert, J. Jordanov and E.K.H. Roth, *J. Am. Chem. Soc.*, 114 (1992) 5693.
- 24 D.J. Darensbourg, *Adv. Organomet. Chem.*, 21 (1982) 113.
- 25 J.R. Morrow, E.L. Tonker and J.L. Templeton, *J. Am. Chem. Soc.*, 107 (1985) 6956.
- 26 P.N. Dickson and D.W. Margerum, *Anal. Chem.*, 58 (1986) 3153.