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# Nucleophilic attack at the five-coordinate anion $[Mn(CO)_3(3,5-di-tert-butyl-catecholate)]^-$ controlled by electronic and steric effects

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#### Abstract

The five-coordinate anion  $[Mn(CO)_4(DBCat)]$  has been found to undergo nucleophilic CO substitution reactions with  $L = PR_4$ ,  $P(OR)_4$  producing the dicarbonyl derivatives  $[Mn(CO)_2(L)(DBCat)]$ . The reaction yield is higher for better nucleophiles such as  $L = PEt_4$  and  $P(OEt)_4$ ; the latter species reacts quantitatively even when added in an equivalent amount. Contrary to this, bulky phosphines with the cone angle  $\theta \ge 145^\circ$ , namely  $L = PPh_4$ ,  $PCy_{44}$  do not show this reaction but interact reversibly with  $[Mn(CO)_4(DBCat)]$  at low temperatures to give the six-coordinate adducts  $\{Mn(CO)_4(DBCat)+L\}$ . For L = pyridine the corresponding adduct is already formed at noom temperature. Similarly,  $[Mn(CO)_2\{P(OEt)_4\}(DBCat)\}$  takes up reversibly  $P(OEt)_4$ . The spectroscopic and redox properties of the adducts closely correspond with those of the invariably six-coordinate anions  $[Re(CO)_{4-n}(L)_n(DBCat)\} = (n = 1, 2)$ . The uptake of a Lewis base by  $[Mn(CO)_4(DBCat)]$  is facilitated by an electrophilic attack at the oxygen lone pairs of the  $\sigma, \pi$ -donor DBCat ligand Examples are the anions  $[Mn(CO)_4(L)(DBCat+BF_4)] = (L = THF, PPh_4)$  and  $[Mn(CO)_4(PPh_4)(DBCat+CS_2)]$  which are inherently stable at ambient temperature. This reactivity is closely related to the DBCat-localized 1e oxidation of  $[Mn(CO)_4(DBCat)]$  producing six-coordinate radicals  $[Mn(CO)_4(L)(DBSQ)]$ . The electrophilic attack of  $CS_2$  at the DBCat ligand has also been documented by the conversion of  $[Mn(CO)_4(DBCat)]$  in the absence of PPh\_4 to the trithiocarbonate complex  $[Mn(CO)_4(S_2CS)]$  and uncoordinated 4,6-di-tert-butyl-1,3-benzdioxol-2-thione. (© 1998 Elsevier Science S.A.

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#### **I. Introduction**

During the last decade there has been permanent interest in reactivity and bonding properties of coordinatively unsaturated, formally '16 electron' complexes of low valent (d<sup>6</sup>) transition metals with  $\sigma, \pi$ -donating redox active chelate ligands (ChL). Examples are (i) carbonyl complexes  $|M(CO)_3(ChL)|^2$ , M = Cr, Mo, W, ChL = catecholate [1-3], benzene-1,2-dithiolate [4,5], oxidophenylamido [6] and phenylenediamido [6] ligands;  $[M(CO)_3(ChL)]^{\sim}$ . M = Mn, ChL = catecholate [7-9]; M = Mn, Re, ChL =  $\alpha$ diimine (or its 2e reduced ene-1.2-diamide form) [10–17];  $[Ru(CO)_2(L)(\alpha - dimine)] = [18-20], and (ii) non-car$ bonyl complexes  $[M(triphos)(catecholate)]^+$  (M = Co.Rh, Ir) [21,22] and [Cp\*M(ene-1,2-diamide)] (M = Rh. Ir) [23]. The characteristic feature of these complexes is the strong electron-releasing effect of the ChL ligand in a low effective oxidation state, which decreases the electronic unsaturation of the metal centre. Those of the above complexes which possess a less extensive  $\pi$ -delocalization within the

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M(ChL) metallacycle are in general more apt for coordination of Lewis bases [3,10,12,13,17] and for oxidative addition of electrophiles [13,21,23,24]. As a typical example, the anion [Mn(CO)<sub>3</sub>(2,2'-bipyridine)]<sup>--</sup> remains inert in acetonitrile [15] and/or in the presence of CO<sub>2</sub> [13] whereas the corresponding less  $\pi$ -delocalized [12,17] anion [Re(CO)<sub>3</sub>(2,2'-bipyridine)]<sup>--</sup> takes up acetonitrile even at ambient temperature [11,13], and is also well known as an efficient electrocatalyst of the CO<sub>2</sub> reduction [13]. Similarly, the fully  $\pi$ -delocalized complex [Co(triphos)(DBCat)]<sup>+</sup> (DBCat = 3,5-di-tert-butylcatecholate) [22] does not react with O<sub>2</sub> whereas a great variety of catecholate oxidation and oxygenation reactions have been reported [21] for significantly more valence-localized derivatives [M(triphos)-(DBCat)]<sup>+</sup> (M = Rh, Ir) [22].

The reactivity of the above complexes is determined by an intriguing interplay of electronic and steric factors and can be tuned by variation of both the metal centre [1-3,12,22-24] and the (formally 2e reduced) ChL ligand [2,3,9,12, 17,23]. Examples will be discussed hereafter. It is obvious

that further combined crystallographic, spectroscopic (e.g. resonance Raman [9,17,22]), electrochemical [8,10–16,18–21,23], theoretical [17,23] and reaction studies of this important class of compounds are needed for a better understanding and control of their bonding properties and reactivity patterns.

This study is a part of the systematic investigation of the interesting five-coordinate anion  $[Mn(CO)_3(DBCat)]^-$ . Previous reports have dealt with its synthesis, X-ray structure, spectroscopic and bonding properties, and redox behaviour [7–9,25]. Contrary to this, the intriguing reactivity of the anionic complex toward nucleophiles (Lewis bases) and electrophiles (Lewis acids) has merely been mentioned [9] but not further investigated. These data are reported herein, allowing a comparison with the behaviour of the six-coordinate derivatives  $[Re(CO)_{4-n}(L)_n(DBCat)]^-$  (n=1-2) [26], and with the previously examined reactivity of the closely related isoelectronic complexes  $[M(CO)_{3-}(DBCat)]^{2-}$  (M = Cr. Mo, W) [1–3].

#### 2. Experimental

#### 2.1. Materials and preparations

All manipulations and reactions were carried out on a vacuum line or under an atmosphere of dry argon or nitrogen, using standard Schlenk techniques.

 $Mn_2(CO)_{10}$  (Strem) was purified by vacuum sublimation. 3.5-Di-tert-butyl-1,2-benzoquinone, DBQ (Aldrich) was recrystallized from n-heptane.  $PCy_3$ ,  $PEt_3$ ,  $PPh_3$  and ferrocene (Fc) (all BDH), were used as purchased.  $P(OEt)_4$ (Fluka) was distilled under reduced pressure from  $CaH_2$ .  $P(OPh)_3$  (Fluka) was dissolved in  $CH_2Cl_2$  and degassed on a vacuum line prior to use.  $[Cp_2Fe]BF_4$  [27],  $PPN[Mn(CO)_3(DBCat)] > 2C_6H_6$  [7],  $PPN[Mn(CO)_4$ -( $PPh_3$ )] [28] and  $PPN[Mn(CO)_4(S_2CS)]$  [29] were prepared by literature methods.  $Bu_4NPF_6$  (Fluka) was recrystallized twice from absolute ethanol, dried under vacuum at 343 K for 10 h, and stored under an atmosphere of dry argon.

Solvents (all of spectrograde quality) were freshly distilled under anaerobic conditions. THF and  $CH_2Cl_2$  (both Janssen) were distilled from a Na/benzophenone mixture and  $P_2O_5$ , respectively. Pyridine (Merck) was dried by refluxing with solid KOH, followed by fractional distillation. Carbon disulphide,  $CS_2$  (Merck) was purified by standing over  $Br_2$  (0.5 ml per 1 l of  $CS_2$ ) for 4 h, followed by threefold shaking with aqueous KOH and stirring with Cu turnings to remove unreacted bromine; finally it was dried by standing over  $CaCl_2$ , followed by distillation from  $P_2O_5$ .

# 2.2. Spectroscopic and electrochemical measurements and instrumentation

<sup>1</sup>H. <sup>13</sup>C and <sup>31</sup>P NMR spectra were obtained on Bruker AM 400 and Bruker AMX 300 spectrometers. Chemical shifts were calibrated against the solvent as a reference. Hewlett Packard 8452 A diode array and Cary 4 spectrophotometers were used to record electronic spectra. UV–Vis spectra at low temperatures were obtained with a Leybold Heraeus ROK 10-300 refrigerator-controlled helium cryostat. The sample solutions in standard 1 cm quartz cuvettes (Hellma) were sealed under high vacuum and placed in a home-made Cu sample holder. The IR spectra were recorded on Bio-Rad FTS 7 and Philips PU 9800 FTIR spectrometers (accuracy of 2 and 4 cm<sup>-1</sup>, respectively). The low-temperature IR measurements were performed using an Oxford Instruments DN 1704/54 liquid-nitrogen cryostat. The mass spectra were obtained on a Jeol JMS-D100 spectrometer.

The cyclic voltammetric (CV) experiments were carried out in a gastight single-compartment cell equipped with a 1 mm Pt disk working. Ag wire pseudoreference and Pt gauze auxiliary electrodes. The surface of the working electrode was carefully polished with a 0.25  $\mu$ m diamond paste. IR spectroelectrochemistry was performed with a previously described optically transparent thin-layer electrolytic (OTTLE) cell [30]. The potential control was achieved with PAR Model 283 and PA4 (EKOM) potentiostats. The redox potentials in this article are referred to the  $E_{1/2}$  value of the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple used as an internal reference system [31]. The CV samples were ca. 1 mM in the Mn complexes and 10<sup>-1</sup> M in Bu<sub>4</sub>NPF<sub>0</sub>.

#### **3. Results**

#### 3.1. Substitution reactions of [Mn(CO) (DBCat)] — with PR , and P(OR) ,

On addition of one equiv. of P(OEt), at room temperature. the wine-red colour of the CH<sub>3</sub>Cl<sub>3</sub> solution of the stable fivecoordinate anion [Mn(CO)<sub>3</sub>(DBCat)]<sup>\*</sup> turned instantaneously orange-red; at the same time evolution of CO gas bubbles was observed. The IR spectrum of the resulting solution showed in the carbonyl-stretching region two intense absorption bands at 1909 and 1821 cm<sup>-1</sup> with almost identical intensities and bandwidths. No splitting of the low-wavenumber band was observed within the temperature interval of 293–183 K. The v(CO) bands of  $|Mn(CO)_3(DBCat)|$ at 1998 and 1891 (broad)  $\operatorname{cm}^{-1}$  [7,9] disappeared completely. The <sup>M</sup>P NMR spectrum of the product in CD<sub>2</sub>Cl<sub>2</sub> exhibited a new signal at 215.8 ppm due to coordinated P(OEt)<sub>3</sub>, which represents a downfield shift by 76.6 ppm relative to the <sup>31</sup>P signal of free P(OEt)<sub>3</sub>. These data point to a facile formation of the substituted dicarbonyl derivative  $[Mn(CO)_{2}{P(OEt)_{3}}(DBCat)]^{\sim}(Eq. (1)).$ 

 $|Mn(CO)_{3}(DBCat)|^{-} + P(OEt)_{3}$ 

 $\rightarrow [Mn(CO)_2 \{P(OEt)_3\}(DBCat)]^{-} + CO \quad (1)$ 

As demonstrated by the IR spectrum, the same product was formed at ambient temperature even when a large excess of  $P(OEt)_3$  was used. The orange-red colour of  $|Mn(CO)_3|$  $\{P(OEt)_3\}(DBCat)\}^-$  has its origin in the presence of two intense absorption bands in the visible spectral region at 416 nm ( $\varepsilon_{max} = 5500 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 514 nm ( $\varepsilon_{max} =$ 4200 M<sup>-1</sup> cm<sup>-1</sup>). These bands are the higher-energy equivalents of the two visible absorption bands of parent  $[Mn(CO)_3(DBCat)]^{\circ}$ , which have been assigned to the  $d_{\pi} \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  electronic transition, respectively [9]. The  $\pi(HOMO) \rightarrow \pi^*(LUMO)$  transition, which possesses some DBCat  $\rightarrow$  Mn CT character [9,17]. is particularly indicative for the five-coordinate geometry of the complexes  $[Mn(CO)_{3-n}(L)_n(DBCat)]^-$  (n = 0, 1) [9]. Substitution of one CO ligand by the stronger  $\sigma$ -donor and weaker  $\pi$ acceptor  $P(OEt)_3$  ligand to give  $[Mn(CO)_2 \{P(OEt)_3\}$ -(DBCat)]  $\bar{}$  apparently destabilizes the  $\pi^*$  LUMO relative to the  $\pi$  HOMO and to the set of occupied d<sub> $\pi$ </sub> orbitals, and is responsible for the high-energy shift of both visible absorption bands.

The dicarbonyl derivative  $[Mn(CO)_2(L)(DBCat)]$ was also formed with  $L = PEt_3$ . However, an excess of  $PEt_3$ was needed to produce  $[Mn(CO)_2(PEt_3)(DBCat)]^{-1}$  quantitatively. In a typical experiment, a mixture of PEt<sub>3</sub>:THF = 1:4 (vol./vol.) was added dropwise to  $[Mn(CO)_{3}]$ (DBCat)]", resulting in a yellow-coloured solution.  $[Mn(CO)_2(PEt_3)(DBCat)] = exhibits two v(CO) bands at$ 1875 and 1780 cm<sup>-1</sup>, indicating a significantly smaller average C = O stretching constant [12.32],  $k_{\rm CO} = 1350$  N m<sup>-1</sup>. relative to that of less electron-rich [Mn(CO)<sub>2</sub>{P(OEt)<sub>3</sub>}-(1405 N m<sup>-1</sup>). The  $d_{\pi} \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$ (DBCat) absorption bands of [Mn(CO)<sub>2</sub>(PEt<sub>3</sub>)(DBCat)] are shifted to a higher energy in comparison with the P(OEt), derivative:  $\lambda_{max} = 344$  and 424 nm (in THF), respectively. This trend fully agrees with the proposed [9] bonding situation in the five-coordinate anions  $[Mn(CO)_{\lambda}]_{n}(L)_{n}$ (DBCat) = (n = 0, 1),

For  $L = P(OPh)_{3}$ , the dicarbonyl anion  $[Mn(CO)_{2^{-1}} \{P(OPh)_{3}\}(DBCat)]^{-1}$  (with  $\nu(CO)$  bands at 1925 and 1842 cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>;  $\bar{k}_{CO} = 1433$  N m<sup>-1</sup>) always existed in equilibrium with parent  $[Mn(CO)_{3}(DBCat)]^{-1}$ , regardless a large excess of  $P(OPh)_{3}$  added to the reaction solution.

 $[Mn(CO)_{3}(DBCat)]^{-1}$  remained completely stable in the presence of bulky PPh<sub>3</sub> or PCy<sub>3</sub> with the Tolman's cone angles [33,34]  $\theta = 145 \pm 2^{\circ}$  and  $179 \pm 10^{\circ}$ , respectively. In order to further probe the coordination of PPh<sub>3</sub>, the synthesis of  $[Mn(CO)_{2}(PPh_{3})(DBCat)]^{-1}$  was also attempted via 2e oxidative addition of one equiv. of 3,5-di-tert-butyl-benzoquinone (DBQ) to the anion  $[Mn(CO)_{4}(PPh_{3})]^{-1}$  (Eq. (2)). The instantaneous reaction however only yielded  $[Mn(CO)_{3}(DBCat)]^{-1}$ , as was evidenced by IR spectroscopy (Eq. (3)).

$$\{Mn(CO)_4(PPh_3)\}^+ + DBQ$$

$$\rightarrow$$
 [Mn(CO)<sub>2</sub>(PPh<sub>3</sub>)(DBCat)] + 2CO (2)

$$[Mn(CO)_4(PPh_3)]^{-} + DBQ$$

$$\rightarrow [Mn(CO)_3(DBCat)]^{-} + PPh_3 + CO \quad (3)$$

Further clear evidence for the non-existence of  $[Mn(CO)_2(PPh_3)(DBCat)]^-$  was obtained from the le reduction of the 18e radical complexes  $[Mn(CO)_{4-n}-(PPh_3)(DBSQ)]$  (n=1, 2; DBSQ=3.5-di-tert-butyl-1,2-benzosemiquinone) in the presence of excess PPh\_3 [25]. The only carbonyl reduction product was in both cases again  $[Mn(CO)_3(DBCat)]^-$  [25]. The instantaneous dissociation of the PPh\_3 ligand(s) from the primary reduction products is thus in complete agreement with the unsuccessful attempts to generate  $[Mn(CO)_2(PPh_3)(DBCat)]^-$  via Eqs. (1) and (2).

### 3.2. Reversible formation of six-coordinate adducts $\{|Mn(CO)_{3-n}(L)_n(DBCat)\} \in L\}^- (n=0, 1)$

#### 3.2.1. IR and UV-Vis spectroscopic studies

The dark red solid  $[Mn(CO)_3(DBCat)]^-$  turned yellow on dissolving in pyridine at room temperature. In the IR spectrum (see Fig. 1) three separate  $\nu(CO)$  bands of comparable intensities appeared at 1995, 1885 and 1862 cm<sup>-1</sup>  $(\tilde{k}_{CO} = 1481 \text{ N m}^{-1})$ . This band pattern unambiguously excludes the formation of the dicarbonyl product  $[Mn(CO)_2(py)(DBCat)]^{\sim}$ . On the other hand, the lower wavenumbers of the  $\nu(CO)$  bands and, hence, the smaller force constant  $k_{CO}$  compared with that of  $|Mn(CO)_3|$ (DBCat)] clearly show that the pyridine donor is present in the coordination sphere of Mn. As a result of the pyridine uptake, the two-band  $(A'_{(1)} + nearly degenerate A'' and$  $A'_{(2)}$ )  $\nu(CO)$  pattern displayed by the fluxional [9] [Mn(CO)<sub>3</sub>(DBCat)] molecule converts to that exhibited by the related six-coordinate anions  $[Re(CO)_{1}(L)]$ . (DBCat)]  $(L = THF, PPh_3)$  [26], with the two lowwavenumber A" and A'<sub>(2)</sub> modes separated by  $\Delta \tilde{\nu} = 15$ -30 cm<sup>-1</sup>. Similarly to [Mn(CO)<sub>3</sub>(DBCat)] in pyridine. the anions  $[Re(CO)_3(L)(DBCat)]$  are also yellow-coloured owing to the presence of a relatively weak absorption



Fig. 1. IR spectra in the  $\nu$ (CO) region recorded at T = 293 K. Solid line: the tive-coordinate anion {Mn(CO)}(DBCat) } in neat CH<sub>2</sub>Cl<sub>2</sub>. Dashed line: the six-coordinate adduct {{Mn(CO)}(DBCat)} py} in neat pyridine.

band in the UV-Vis spectra around 400 nm [26]. This band has been assigned [9,26] to a symmetry-allowed but overlapforbidden  $\pi^* \rightarrow \sigma^*$  LMCT transition, the  $\pi^*$  orbital being predominantly the 3b<sub>1</sub> HOMO of the DBCat ligand (see Ref. [9], in particular Scheme ! therein). This transition is a prominent feature of these photoreactive [26] six-coordinate Re anions and has no analogy in the photostable five-coordinate anions [Mn(CO)<sub>3-n</sub>(L)<sub>a</sub>(DBCat)]<sup>-</sup> (n=0, 1) [9]. Importantly, the UV-Vis spectrum of [Mn(CO)<sub>3</sub>-(DBCat)]<sup>-</sup> dissolved in neat pyridine also exhibits such a lowest absorption band at  $\lambda_{max} = 434$  nm ( $\varepsilon_{max} =$ 2200 M<sup>-1</sup> cm<sup>-1</sup>). Excitation into the corresponding electronic transition caused, in agreement with its assumed LMCT character, fast irreversible decomposition of the tricarbonyl anion.

In order to examine whether pyridine coordinates reversibly to  $[Mn(CO)_3(DBCat]^-$ , the yellow solution of the anion in neat pyridine was degassed on a vacuum line and pyridine was subsequently distilled off completely. The resulting dark red solid was characterized as  $[Mn(CO)_3(DBCat)]^-$  by its IR spectrum as well as by the UV–Vis spectrum of its characteristically wine-red-coloured solution in CH<sub>2</sub>Cl<sub>2</sub>. These results point to complete recovery of the five-coordinate anion. In addition to this, comparison of the UV–Vis spectra of  $3.5 \times 10^{-4}$  M [Mn(CO)<sub>3</sub>(DBCat)]<sup>-</sup> in neat CH<sub>2</sub>Cl<sub>2</sub> and in the 1.0 M solution of pyridine in CH<sub>2</sub>Cl<sub>2</sub> at T = 293 K revealed that in the latter case ca. 75% of the anionic complex reacted with pyridine.

In essence, the above experimental results are consistent with a reversible uptake of pyridine by  $\{Mn(CO)_{3}-(DBCat)\}^{-}$ , producing a six-coordinate adduct formulated as  $\{\{Mn(CO)_{3}(DBCat)\}^{+}py\}^{-}$ .

Formation of corresponding adducts ([Mn(CO)] - $(DBCat) | L = (L = PPh_3, PCy_3)$  was studied by IR spectroscopy at variable temperatures (Fig. 2). Fig. 2(a) reveals that there is only a little change in the  $\nu(CO)$  region on cooling the  $10^{-3}$  M solution of  $(Mn(CO)_3(DBCat))^{-1}$  in neat CH<sub>2</sub>Cl<sub>2</sub> down to 193 K. The IR peak at 1998 cm<sup>-1</sup> belonging to the A'<sub>(1)</sub>,  $\nu$ (CO) mode shifts to 2001 cm<sup>-1</sup>. The broad  $\nu(CO)$  band at 1891 cm<sup>-1</sup> slightly narrows and two maxima show up at 1894 and 1883 cm<sup>-1</sup> owing to a better resolution of the A" and A'<sub>(2)</sub>  $\nu$ (CO) modes. On the contrary, the IR spectra of the 10<sup>-3</sup> M solution of  $[Mn(CO)_3(DBCat)]^-$  in CH<sub>2</sub>Cl<sub>2</sub> changed substantially on cooling in the presence of  $10^{-1}$  M PPh<sub>3</sub> or PCy<sub>3</sub> (Fig. 2(b) and (c)). The  $\nu$ (CO) bands of [Mn(CO)<sub>3</sub>(DBCat)]<sup>-</sup> were replaced with retention of isosbestic points by new bands of {[Mn(CO)<sub>3</sub>(DBCat)]·L}<sup>=</sup> at 2001, 1904 and 1867 cm<sup>-1</sup> for  $L = PPh_3$ , and at 1993, 1882 and 1853 cm<sup>-1</sup> for  $L = PCy_3$ . These spectral changes are completely reversible, as was manifested by the conversion of the IR spectra of  $\{[Mn(CO)_3(DBCat)] \cdot L\} \in (L = PPh_3, PCy_3)$  back to the initial spectrum of [Mn(CO)3(DBCat)] on warming the solution to 293 K. It is noteworthy that the difference between the wavenumbers of the A" and A'<sub>(2)</sub>  $\nu$ (CO) modes of the adducts { [Mn(CO), (DBCat) ]  $\cdot$  L}  $\neg$ ,  $\Delta \tilde{\nu} = 27$  and 29 cm  $\neg$  '



Fig. 2. IR spectra in the  $\rho$ (CO) region recorded at T = 293 K (dashed lines) and at 193 K (solid lines). (a) 10<sup>-1</sup> M [Mn(CO)<sub>3</sub>(DBCat)] in neat CH<sub>2</sub>Cl<sub>2</sub>; (b) 10<sup>-3</sup> M [Mn(CO)<sub>3</sub>(DBCat)] in CH<sub>3</sub>Cl<sub>3</sub>/10<sup>-1</sup> M PCy<sub>3</sub>; (c) 10<sup>-3</sup> M [Mn(CO)<sub>3</sub>(DBCat)] in CH<sub>3</sub>Cl<sub>3</sub>/10<sup>-1</sup> M PPh<sub>3</sub>. The low temperature spectra in (b) and (c) correspond to the six-coordinate adducts {[Mn(CO)<sub>3</sub>(DBCat)] · PR<sub>3</sub>] = (R = cyclohexyl, phenyl).

for L=PPh<sub>3</sub> and PCy<sub>3</sub>, respectively, is very close to  $\Delta \tilde{\nu} = 23 \text{ cm}^{-1}$  for L=py (see above). However, the  $\bar{k}_{CO}$  force constant of [Mn(CO)<sub>3</sub>(DBCat)] = (1500 N m<sup>-1</sup>) decreased owing to the association with L only for L=PCy<sub>3</sub> ( $\bar{k}_{CO} = 1474 \text{ N m}^{-1}$ ) whereas it remained almost unchanged for L=PPh<sub>3</sub> ( $\bar{k}_{CO} = 1496 \text{ N m}^{-1}$ ). The latter phenomenon might have its origin in averaging of the particular energy-factored force constants  $k_{CO}$  and  $k_{COCO}$ .

Formation of a six-coordinate adduct was also expected for the dicarbonyl anion  $[Mn(CO)_2{P(OEt)_3}(DBCat)]^$ in the presence of excess  $P(OEt)_3$ . In this case UV-Vis spectra of  $8 \times 10^{-8}$  M  $[Mn(CO)_2{P(OEt)_3}(DBCat)]^-$  in  $CH_2Cl_2:P(OEt)_3 = 4:1$  (vol./vol.) were recorded within the temperature interval  $193 \le T \le 293$  K. At T = 293 K, the UV-Vis spectrum was identical with that of pure  $[Mn(CO)_2{P(OEt)_3}(DBCat)]^-$  in neat CH<sub>2</sub>Cl<sub>2</sub> (see Section 3.1.). While the latter spectrum did not change significantly with temperature, cooling of the red-orange solution of  $[Mn(CO)_2{P(OEt)_3}(DBCat)]$ containing excess P(OEt)<sub>3</sub> to 230 K caused gradual rise of two new absorption bands at 413 nm ( $\varepsilon_{max} = 2200 \text{ cm}^{-1}$ ) and 333 nm  $(\varepsilon_{max} = 6500 \text{ cm}^{-1})$  with retention of the isosbestic point at 362 nm. Elevating again the temperature to T = 293 K led to complete reappearance of the characteristic absorption bands of  $[Mn(CO)_{2}{P(OEt)_{3}}(DBCat)]^{-1}$  at 416 and 514 nm. This behaviour corresponds with a reversible generation of the six-coordinate adduct  $\{ Mn(CO)_{3} \{ P(OEt)_{3} \} (DBCat) \}$ .  $P(OEt)_3$  which is the single species present in the solution at  $T \le 230$  K. The lowest absorption band of  $\{[Mn(CO)_2 \{P(OEt)_3\} (DBCat)] \cdot P(OEt)_3\}^{-}$  at 413 nm is assigned to the  $\pi^* \rightarrow \sigma^*$  LMCT transition [9], in analogy with the adduct  $\{|Mn(CO)_3(DBCat)| \cdot py\}$  (see above) and with the related six-coordinate anion [Re(CO)<sub>2</sub>- $(PPh_3)_2(DBCat)$ ] = [26].

#### 3.2.2. Cyclic voltammetry

In general, the complexes  $\{Mn(CO)_{3-n}(L)_n(DBCat)\}^{-1}$ (n=0, 1) undergo one-electron DBCat-localized oxidation and one-electron reduction localized on the Mn<sup>1</sup> centre  $\{8,25\}$ . The oxidation is accompanied by an uptake of a Lewis base L, e.g. a donor solvent, producing six-coordinate complexes  $\{Mn(CO)_3(L)(DBSQ)\}$  which can be further oxidized to the corresponding  $\{Mn(CO)_3(L)(DB-Quinone)\}^{+}$  species  $\{8,9,25,35\}$  (see Fig. 3).

Valuable information about the tendency of  $[Mn(CO)_3$ -(DBCat)] to associate with Lewis bases L prior to its oxidation could be obtained from cyclic voltammograms recorded in neat CH<sub>2</sub>Cl<sub>2</sub> ( $E_{p,a} = -0.44$  V), in THF ( $E_{p,a} = -0.63$  V), in CH<sub>2</sub>Cl<sub>2</sub>/excess PPh<sub>4</sub> ( $E_{p,a} = -0.94$  V) [8.25], and in neat pyridine ( $E_{p,a} = -0.87$  V; see Fig. 3). The negative shift of the anodic peak potential correlates with the increasing stability of the 18e oxidation products [Mn(CO)<sub>3</sub>(L)(DBSQ)] (L=THF, PPh<sub>4</sub>, py) relative to that of coordinatively unsaturated [Mn(CO)<sub>3</sub>(DBSQ)] in neat CH<sub>2</sub>Cl<sub>2</sub> [8.25.35].

Fig. 3. Cyclic voltammogram of  $[Mn(CO)_3(DBCat)] = (ca. 1 mM)$  in pyridine. The anodic peak at  $E_{p,a} = \pm 0.11$  V corresponds to the chemically irreversible 1e oxidation of  $[Mn(CO)_3(py)(DBSQ)]$ . Conditions:  $10^{-1}$  M Bu<sub>4</sub>NPF<sub>6</sub>, 1 mm Pt disk working electrode, T = 293 K, scane rate v = 100 mV s<sup>-1</sup>. Inset: FTIR absorption difference spectrum recorded during the electro-oxidation of  $\{[Mn(CO)_3(DBCat)], py\}$  to  $\{Mn(CO)_3(DBSQ)\}$  in neat pyridine at  $E_{1/2} = -0.90$  V within the IR OTTLE cell [30] at T = 293 K.

The latter result is not surprising taking into account the spectroscopically established formation of the six-coordinate adduct {[Mn(CO)<sub>3</sub>(DBCat)]·py}<sup>-</sup> at room temperature (see Section 3.2.1.). The one-electron oxidation of this adduct gives the six-coordinate radical [Mn(CO)<sub>3</sub>(py)-(DBSQ)]. The corresponding electron transfer to the anode is thus not accompanied by any significant structural change and the oxidation is therefore electrochemically reversible. The same argument applies for the five-coordinate redox couple [Mn(CO)<sub>3</sub>(DBCat)] =/[Mn(CO)<sub>3</sub>(DBSQ)] in neat  $CH_2Cl_2$  [8]. On the other hand, the spectroscopic results document that the six-coordinate adducts {[Mn(CO)<sub>3</sub>-(DBCat)  $|\cdot L$   $(L = THF, PPh_3)$  do not exist at room temperature (see Section 3.2.1.). The coordination of the sixth ligand L, present in the solvation sphere of [Mn(CO)<sub>3</sub>(DBCat)]<sup>\*</sup> at the very moment of the electrode reaction, thus becomes induced by the oxidation. The corresponding structural change between the five- and six-coordination geometries results in a large reorganization energy. slowing down the heterogeneous electron transfer. Hence. the oxidation of [Mn(CO)<sub>3</sub>(DBCat)]<sup>-</sup> in THF and in CH<sub>2</sub>Cl<sub>2</sub>/excess PPh<sub>3</sub> is electrochemically quasireversible.

The redox behaviour of the dicarbonyl anion  $[Mn(CO)_2 {P(OEt)_3}(DBCat)]^-$  is very similar to that of  $[Mn(CO)_3(DBCat)]^-$ . In CH<sub>2</sub>Cl<sub>2</sub>/excess P(OEt)<sub>3</sub> at room temperature, the one-electron oxidation of the former anion (weakly interacting with P(OEt)<sub>3</sub> but not forming the six-coordinate adduct { $[Mn(CO)_2{P(OEt)_3}(DBCat)]^-$  P(OEt)<sub>3</sub>]<sup>-</sup>, see Section 3.2.1.) takes place at  $E_{p,a} =$ 





Fig. 4. Cyclic voltammogram of  $\{Mn(CO)_2\{P(OEt)_3\}(DBCat)\}^+$  (ca. 1 mM) in CH<sub>2</sub>Cl<sub>2</sub>/P(OEt)<sub>3</sub>=4:1 (vol./vol.). Conditions identical with those listed in Fig. 3. For description see Section 3.2.2.

= 1.17 V (see Fig. 4). As expected, this step, producing the stable radical {Mn(CO)<sub>2</sub>{P(OEt)<sub>3</sub>}<sub>2</sub>(DBSQ)}, is electrochemically quasireversible:  $\Delta E_p = 155 \text{ mV}$  versus 90 mV for Fc/Fc<sup>+</sup>;  $I_{p,a}^{oxl}$ ;  $I_{p,a}^{oxl} = 0.77$ .  $I_{p,a}^{oxl}$  belongs to the subsequent one-electron oxidation of {Mn(CO)<sub>2</sub>{P(OEt)<sub>3</sub>}<sub>2</sub>-(DBSQ)} at  $E_{p,a} = -0.31 \text{ V}$  producing the corresponding stable cationic DBQ complex, which is electrochemically reversible.

The cyclic voltammogram of [Mn(CO)<sub>2</sub>[P(OEt)<sub>3</sub>]-(DBCut) = recorded in  $CH_2Cl_2$  in the absence of free P(OEt)<sub>3</sub> is considerably more complicated (Fig. 5). The most negative anodic peak  $A_0$  at  $E_{p,a} = -0.60$  V versus Fc/ Fe \* corresponds to the DBCat-localized 1e oxidation of the parent anion, which primarily produces the coordinatively unsaturated radical [Mn(CO)<sub>2</sub>[P(OEt)<sub>2</sub>](DBSO)]. This anodic step is chemically irreversible at  $v = 100 \text{ mV s}^{-1}$ . The rather large positive potential shift of 570 mV relative to the  $E_{p,a}$  value of  $[Mn(CO)_2 \{P(OEt)_3\} (DBCat)]^{-1}$  in the presence of free P(OEt), testifies to a close resemblance with the oxidation of  $[Mn(CO)_3(DBCat)] =$  in CO-free  $CH_2Cl_2[8]$ . The five-coordinate radical [Mn(CO)<sub>2</sub>{P(OEt)<sub>3</sub>}(DBSQ)] is apparently very unstable and rapidly decomposes to give the six-coordinate radicals  $[Mn(CO)_2[P(OEt)_1]_2$ (DBSQ) and  $[Mn(CO)_3{P(OEt)_3}(DBSQ)]$  by an unknown EC mechanism. Their presence in the oxidized solution is confirmed by the subsequent more positive redox couples  $[Mn(CO)_2[P(OEt)_1]_2(DBSQ)]/[Mn(CO)_2]$  $\{P(OEt)_3\}_2(DBQ)\}^+$  at  $E_{1/2} = -0.39 V (B/B' in Fig. 5;$ see also Fig. 4) and [Mn(CO)<sub>3</sub>[P(OEt)<sub>3</sub>]-(DBSQ)]/  $[Mn(CO)_{3}[P(OEt)_{3}](DBQ)]^{+}$  at  $E_{1/2} = -0.10 V (C/C')^{-1}$ in Fig. 5). The latter value is close to  $E_{1/2} = +0.02$  V of the corresponding redox couple [Mn(CO)<sub>3</sub>(PPh<sub>3</sub>)(DBSQ)]/



Fig. 5. Cyclic voltammogram of  $\{Mn(CO)_2\{P(OEt)_1\}(DBCat)\}^{-1}$  (ca. 1 mM) in neat CH<sub>2</sub>Cl<sub>2</sub>. Conditions identical with those listed in Fig. 3. For description see Section 3.2.2.

[Mn(CO)<sub>3</sub>(PPh<sub>3</sub>)(DBQ)]<sup>+</sup> [25]. On the reverse scan, the one-electron reduction of [Mn(CO)<sub>2</sub>{P(OEt)<sub>3</sub>}<sub>2</sub>(DBSQ)] as the major secondary oxidation product is found at  $E_{p,c} = -1.23$  V (cathodic peak A' in Fig. 5; see also Fig. 4) whereas [Mn(CO)<sub>3</sub>{P(OEt)<sub>3</sub>}(DBSQ)] reduces at  $E_{p,c} =$ =0.98 V versus Fc/Fc<sup>+</sup> (cathodic peak D' in Fig. 5)<sup>-1</sup>. For comparison, the reduction of [Mn(CO)<sub>3</sub>(PPh<sub>3</sub>)(DBSQ)] has been reported at  $E_{p,c} = -1.085$  V [25].

#### 3.3. Electrophilic attack at the DBCat ligand in [Mn(CO)\_(DBCat)]=

In the preceding sections it was demonstrated that  $[Mn(CO)_3(DBCat)]^-$  is not able to take up PPh<sub>3</sub> at room temperature. It was also shown [9,26,35,37] that le oxidation of the strong  $\pi$ -donor DBCat ligand to the DBSQ radical results in the strongly diminished  $\pi$ -donation towards the Mn centre and, consequently, in the facile coordination of Lewis bases L (THF, PPh<sub>3</sub>, etc.) yielding the stable six-coordinate radicals [Mn(CO)<sub>3</sub>(L)(DBSQ)]. In this respect, an interesting question has arisen whether also an electrophilic attack

<sup>&</sup>lt;sup>1</sup> It is not clear why the cathodic peak D' does not appear on the reverse cathodic scan directly after passing the anodic peak  $A_0$ . As a possible explanation, the minor tricarbonyl radical  $\{Mn(CO)_1\{P(OEt)_1\}(DBSQ)\}$  is not produced parallelly with major  $\{Mn(CO)_2\{P(OEt)_1\}_2(DBSQ)\}$  but in a later stage of the complex EC sequence which may consist of the following steps: (i)  $[Mn(CO)_2\{P(OEt)_1\}(DBCat)] \rightarrow [Mn(CO)_2\{P(OEt)_1\}_1(DBSQ)\} \rightarrow [Mn(CO)_2\{P(OEt)_1\}_2(DBSQ)] \rightarrow [Mn(CO)_2(DBSQ)];$  (iii)  $Mn(CO)_2(DBSQ)] \rightarrow [Mn(CO)_2(DBSQ)]$  $\rightarrow Mn(DBSQ)' + 2 CO(decomp.);$  (iv)  $[Mn(CO)_2\{P(OEt)_1\}(DBSQ)]$  $+ CO \rightarrow [Mn(CO)_4\{P(OEt)_1\}(DBSQ)].$ 

at the DBCat ligand in  $[Mn(CO)_3(DBCat)]^-$  may increase the Lewis acidity of the Mn centre to such an extent that it promotes coordination of a Lewis base.

#### 3.3.1. Coordination of Lewis bases to [Mn(CO)<sub>3</sub>(DBCat)]<sup>-</sup> induced by BF<sub>3</sub>

Strongly Lewis acidic BF<sub>3</sub> was expected to attack efficiently the oxygen atom(s) of the basic DBCat ligand in  $[Mn(CO)_3(DBCat)]^-$  giving rise to the formation of the adduct  $[Mn(CO)_3(DBCat \cdot BF_3)]^-$ . The uptake of BF<sub>3</sub> by relevant organic compounds with nucleophilic hydroxyl groups such as alcohols (ethyleneglycol, benzylalcohol) or acids (oxalic acid) is a well known phenomenon [38]. Similarly, BF<sub>3</sub> attacks the nucleophilic CN<sup>-</sup> ligands in  $[Fe(CN)_5(NO)]^{2+}$  producing  $[Fe(CN \cdot BF_3)_5(NO)]^{2+}$ with considerably higher CN and NO stretching frequencies relative to those of the parent complex [39].

In order to examine whether the adduct  $[Mn(CO)_{3}]$  $(DBCat \cdot BF_3)$  was formed, 1.5 ml of  $BF_3 \cdot Et_3O$  was added dropwise to the  $10^{-2}$  M solution of  $\{Mn(CO)\}$ (DBCat) in THF ( $\nu(CO)$  bands at 1994 and 1891 (broad)  $\operatorname{cm}^{-1}$  [7,9]). The IR spectrum of the resulting yellow solution exhibited two strong  $\nu(CO)$  bands at 2015 and 1928 (broad) cm<sup>-1</sup>. The tendency of the adduct to coordinate Lewis bases was further studied by adding an equivalent amount of PPh<sub>3</sub> to the solution in THF. The IR  $\nu$ (CO) band pattern converted quantitatively to that consisting of a strong (s)  $\nu(CO)$  band at 2022 cm<sup>-1</sup> and two  $\nu(CO)$  bands of medium (m) intensities at 1953 and 1909 cm<sup>-1</sup>. A comparison with the IR spectra of electrochemically generated  $[Mn(CO)_{1}(THF)(DBSQ)] (\nu(CO) at 2029 (s), 1932 (s))$ and 1925 (sh) cm<sup>-1</sup>) [8,9,35] and  $[Mn(CO)_3(PPh_3)]$ - $(DBSO) \mid (\nu(CO) \text{ in THF at } 2025 \text{ (s)}, 1945 \text{ (m) and } 1916$ (m) cm<sup>-1</sup>) [27.35] clearly documents that both THF and **PPh**<sub>1</sub> indeed readily coordinate. The shift in the  $\nu$ (C-O) wavenumber of the DBCat ligand, which should also increase on BF<sub>3</sub> uptake, could not be observed owing to the low intensity of the corresponding IR band of [Mn(CO)<sub>3</sub>(DBCat)] at 1254 cm<sup>-+</sup> [9], obscured by the solvent absorption. The slightly higher wavenumbers and identical patterns of the  $\nu$ (CO) bands of | Mn(CO)<sub>3</sub>(L)(DBSQ) | (L = THF, PPh<sub>3</sub>) relative to the BF<sub>3</sub>-containing products allow the most probable formulation of the latter species as  $[Mn(CO)_3(L)]$ - $(DBCat \cdot BF_3) |$ 

On the other hand, a striking difference exists between the UV–Vis spectra of blue-violet  $|Mn(CO)_3(THF)(DBSQ)|$  [9,35] and blue-green  $[Mn(CO)_3(PPh_3)(DBSQ)]$  [25, 35] that typically exhibit low-lying  $d_{\pi}(Mn) \rightarrow \pi^{\#}$ -(DBSQ) charge transfer (MLCT) transitions, and those of the yellow  $[Mn(CO)_3(L)(DBCat \cdot BF_3)]^-$  complexes which only weakly absorb in the near-UV–Vis spectral region at  $\lambda_{max} = 407$  nm (L = THF) and 380 nm (L = PPh\_3). In this instance, the UV–Vis spectra of the latter two complexes strongly resemble that of the yellow six-coordinate adduct  $\{|Mn(CO)_3(DBCat)| \cdot py\}^-$  (see above), pointing to the same, i.e.  $\pi^* \rightarrow \sigma^*$  LMCT [9], character of the lowest elec-

tronic transition. This result suggests that the catecholate ligand, DBCat, retained its oxidation state.

## 3.3.2. Reactivity of [Mn(CO)<sub>3</sub>(DBCat)] toward PPh<sub>3</sub> induced by CS<sub>2</sub>

The electrophilic reactivity of carbon in carbon disulphide was well established, e.g. in reactions with nucleophilic CN<sup>+</sup>, or with basic PR<sub>3</sub> molecules such as PBu<sub>3</sub> which convert to the zwitterionic adducts  $R_3P^+C(S)S^-$  [40]. Carbon disulphide was therefore chosen as another suitable electrophilic reagent that might promote coordination of Lewis bases to [Mn(CO)<sub>3</sub>(DBCat)]<sup>-</sup>, as was found for BF<sub>3</sub> (see above).

At T = 193 K, a slow reaction between  $\{Mn(CO)\}$ (DBCat) =  $(10^{-2} M)$  and excess PPh<sub>3</sub> in CH<sub>5</sub>Cl<sub>5</sub>/  $CS_3 = 5:1$  (vol./vol.) yielded two carbonyl complexes characterized by IR spectroscopy. The major product exhibited three strong  $\nu$ (CO) bands at 1995, 1915 and 1886 cm<sup>-1</sup>. These wavenumbers correspond to  $k_{\rm CO} = 1509$  N m<sup>-1</sup>. Comparison of these IR data with the  $\nu(CO)$  wavenumbers of the low-temperature adduct  $\{[Mn(CO)_3(DBCat)] \cdot PPh_3\}$  $(\bar{k}_{CO} = 1496 \text{ N m}^{-1}$ , see above) strongly suggests that a similar species was formed. It is formulated as  $[Mn(CO)_3(PPh_3)(DBCat \cdot CS_2)]^{\circ}$ , i.e. with CS<sub>2</sub> bound to the DBCat nucleophilic centre. This assignment gets support (i) from the inherent stability of the tricarbonyl complex even at T = 293 K, where no association of PPh<sub>3</sub> with  $[Mn(CO)_3(DBCat)]^{\sim}$  takes place in the absence of a Lewis acid, and (ii) from the fact that the oxidation of the complex by [Cp<sub>2</sub>Fe]BF<sub>4</sub> yielded exclusively [Mn(CO)<sub>3\*</sub> (PPh<sub>x</sub>)(DBSQ)]. Furthermore, the electrophilic attack of CS, at the DBCat ligand in [Mn(CO)<sub>3</sub>(DBCat)] could be established independently, as described in the next section. Another supporting evidence for the six-coordination geometry of  $|Mn(CO)_{4}(PPh_{4})(DBCat \cdot CS_{2})|$  is provided by its UV=Vis spectrum that exhibits the characteristic weak  $\pi^* \rightarrow r^*$  LMCT band at  $\lambda_{\max} = 390$  nm (see Section 3.2.1.).

The second, minor carbonyl product obtained at T = 193 K is characterized by two  $\nu$  (CO) bands at 1900 and 1809 cm  $^{-1}$  $(\bar{k}_{co} = 1390 \text{ N m}^{-1})$ . It slowly decomposed after warming of the reaction mixture up to ambient temperature. The  $\nu$ (CO) spectral pattern, wavenumbers and the  $\bar{k}_{CO}$  value point to a close relation of this species to the anions  $[Mn(CO)_2(L)(DBCat)] = (L = P(OEt)_3 \text{ and } PEt_3. \text{ see}$ Section 3.1.). However, in view of the fact that the anion [Mn(CO)<sub>2</sub>(PPh<sub>3</sub>)(DBCat)] could not be produced by a CO substitution reaction of  $[Mn(CO)_4(DBCat)]^{-1}$  in the absence of  $CS_2$ , it is reasonable to assign the thermally unstable dicarbonyl complex as [Mn(CO)<sub>2</sub>(PPh<sub>3</sub>)- $(DBCat \cdot CS_2)$  ]  $\square$ . Thus, the replacement of a CO ligand in  $[Mn(CO)_3(DBCat)]$  by PPh<sub>3</sub> is still possible provided the Lewis basicity of the DBCat ligand becomes reasonably reduced on interaction with a Lewis acid.

#### 3.3.3. Reaction of [Mn(CO)<sub>3</sub>(DBCat)] with CS<sub>2</sub>

 $5 \times 10^{-3}$  M [Mn(CO)<sub>3</sub>(DBCat)] underwent a slow thermal reaction in CH<sub>2</sub>Cl<sub>2</sub>/CS<sub>2</sub>=5:1 (vol./vol.) at T= 293 K which was monitored by IR spectroscopy. The  $\nu$ (CO)



Fig. 6. IR spectral changes in the  $\nu(CO)$  region accompanying the thermal reaction of  $|Mn(CO)_3(DBCat)|^-$  with CS<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> at T=293 K to give the trithiocarbonate complex  $|Mn(CO)_4(S_2CS)|^-$ .

bands of the parent anion were completely replaced during 5 h by four  $\nu$ (CO) bands at 2067 (m), 1987 (vs), 1967 (s) and 1924 (s) cm<sup>-1</sup> with the retention of isosbestic points (Fig. 6). Performing the reaction in  $THF/CS_2$  the new  $\nu$ (CO) bands arose at 2059 (m), 1981 (vs), 1963 (s) and 1921 (s) cm<sup>-1</sup>. These wavenumbers can unambiguously be attributed to the trithiocarbonate complex [Mn(CO)<sub>4</sub>- $(S_2CS)$  = [29]. In accordance with the literature [29,41]. the CS stretching modes of the S.S'-coordinated trithiocarbonate ligand were found at 1024, 1012 (both v(C=S)) and 867 ( $v_{sym}$ (C=S)) cm<sup>=1</sup>. No transient curbonyl complex was observed in the course of the reaction. The formation of  $[Mn(CO)_4(S_2CS)]^-$  was further confirmed by its subsequent methylation with  $CH_{1}$ . The  $\nu(CO)$  bands of the  $[Mn(CO)_4(S_2CSCH_3)]$  product were found at 2092 (m). 2014 (vs), 2003 (s) and 1961 (s) cm<sup>-1</sup> (in CH<sub>2</sub>Cl<sub>2</sub>) [29]. The v(C-S) mode of the chelated  $S_2CSCH_1$  ligand was localized at 965 cm<sup>-1</sup>.

The DBCat ligand in { $Mn(CO)_3(DBCat)$ } transformed during the thermal reaction with CS<sub>2</sub> into uncoordinated 4,6di-tert-butyl-1,3-benzdioxol-2-thione (DBBT), as was established by mass and NMR spectroscopy: m/e (%) 264 (55) (M<sup>+</sup>, C<sub>15</sub>H<sub>20</sub>O<sub>2</sub>S), 249 (100) (C<sub>14</sub>H<sub>17</sub>O<sub>2</sub>S), 233 (4), 189 (75) (C<sub>13</sub>H<sub>17</sub>O)<sup>2</sup>; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  (ppm) 1.30 (9H) and 1.40 (9H) ((CH<sub>3</sub>)<sub>3</sub>C=C<sub>4</sub> and (CH<sub>3</sub>)<sub>3</sub>C=C<sub>6</sub>), 7.16 (1H) and 7.19 (1H)  $(C_5-H \text{ and } C_7-H)$ ; <sup>13</sup>C NMR  $(CD_2Cl_2)$  $\delta$  (ppm) 29.91 and 31.65 ( $(CH_3)_3C-C_4$  and  $(CH_3)_3C-C_6$ ), 34.74 and 35.66 ( $(CH_3)_3C-C_4$  and  $(CH_3)_3C-C_6$ ), 105.41 and 120.25 ( $C_5$  and  $C_7$ ), 134.53 and 142.12 ( $C_4$  and  $C_6$ ), 146.50 and 150.09 ( $C_1$  and  $C_3$ ), 184.95 (C=S) <sup>3</sup>. Characteristic IR bands of DBBT due to the O.O-C=S function appeared at 1333 and 984 cm<sup>-1</sup>.<sup>4</sup>

#### 4. Discussion

# 4.1. Formation of $[Mn(CO)_2(L)(DBCat)]^- (L = PR_3, P(OR)_3)$

The five-coordinate anion  $[Mn(CO)_3(DBCat)]^-$  undergoes a CO substitution reaction with  $L = PR_3$  or  $P(OR)_3$ , producing  $[Mn(CO)_2(L)(DBCat)]^-$ . The yield of the reaction strongly depends on the nucleophilic character of L, being higher for nucleophiles with smaller cone angle  $\theta$  and higher basicity. Comparison of the reactivity of various phosphorus ligands reveals that the cone angle plays the major role. Thus, no CO substitution occured for L with  $\theta \ge 145^{\circ}$ . viz. PPh<sub>3</sub> and PCy<sub>3</sub>, regardless of the substantially different basicity of the latter two tertiary phosphines [46]. On the other hand, using the same (large) excess of  $L = PEt_3$  $(\theta = 132 \pm 4^\circ)$  and P(OPh<sub>3</sub>) ( $\theta = 121 \pm 10^\circ$ ) the substitution occurred readily. It led to completion for the somewhat larger but significantly more basic PEt<sub>3</sub> ligand [46] whereas an equilibrium between  $[Mn(CO)_4(DBCat)]^{-1}$  and  $[Mn(CO)_{2^n}]^{-1}$ (L)(DBCat)was observed for the good  $\pi$ -acceptor P(OPh)<sub>3</sub>. This difference in reaction yield is thus due to the influence of the basicity factor. Importantly, for the smallest L in the series, P(OEt)<sub>3</sub> with  $\theta = 109 \pm 2^{\circ}$ , only one equiv. of L was needed for the quantitative conversion of the parent tricarbonyl anion to  $|Mn(CO)_2|P(OEt)_3|(DBCat)|^{\infty}$ .

These results fully agree with those of Palmer et al. [47] on the complex  $Cp_2Ti(CO)_2$  and its monosubstutited derivatives  $Cp_2Ti(CO)(L)$  (L = PR<sub>3</sub>, P(OR)<sub>3</sub>). The CO substitution in that case was also found to proceed faster and with a higher yield for better nucleophiles L. Thus, the reactivity of L possessing very similar cone angle  $\theta$  (P(OEt)<sub>3</sub> versus PMe<sub>3</sub> and P(O-iPr)<sub>3</sub> versus PMePh<sub>2</sub>) increased with their higher basicity. On the other hand, L of similar basicity [46] (PMe<sub>3</sub> versus PBu<sub>3</sub> and P(OEt)<sub>3</sub> versus P(O-iPr)<sub>3</sub>) were found significantly less reactive on increasing their cone angle. Similarly to [Mn(CO)<sub>3</sub>(DBCat)]<sup>--</sup>, the complex  $Cp_2Ti(CO)_2$  remained almost inert toward L = PPh<sub>3</sub>, and no reaction was observed for L = PCy<sub>3</sub> [47].

<sup>&</sup>lt;sup>2</sup> It is noteworthy that elimination of the COS group from the daughter ion of 4.6-di-tert-butyl-1,3-benzdioxol-2-thione (as indicated by the presence of the fragment m/e = 189 in the mass spectrum) mimics the photolytic reactions of this and other thioxocarbonates [42], being thus the specific feature for this group of organic compounds. On the contrary, a substantially different fragmentation pattern has been reported [43] for isomeric 4.6-ditert-butyl-1,3-benzoxathiol-2-one as the alternative reaction product: m/e(%) 264 (20), 249 (100), 221 (5), 205 (4), 193 (10).

<sup>&</sup>lt;sup>4</sup> The C=S group of the unsubstituted derivative 1.3-benzdioxol-2-thione resonates in the <sup>14</sup>C NMR spectrum at  $\delta$  185.40 ppm (in DMSO-d<sub>6</sub>) [44].

<sup>&</sup>lt;sup>4</sup> These IR bands were also found in the IR spectrum of DBBT independently synthesized from the Na<sup>+</sup> salt of DBCat and thiophosgene [45]; they are not present in the IR spectrum of PPN[Mn(CO)<sub>4</sub>(S<sub>2</sub>CS)] produced photochemically from PPN[Mn(CO)<sub>5</sub>] and CS<sub>2</sub> [29].

The CO substitution reaction of  $[Mn(CO)_3(DBCat)]^$ with PR<sub>3</sub> and P(OR)<sub>3</sub> does not occur in the case of the related isostructural complexes  $[M(CO)_3(Cat)]^{2-}$  and  $[M(CO)_{3^-}(DBCat)]^{2-}$  (M=Cr, Mo, W) studied by Darensbourg et al. [1-3]. This result is not surprising in view of the much higher electron density distributed over the  $M(CO)_3$  fragment in the latter case, as documented by the rather low  $\bar{k}_{CO}$ values ranging between 1280 and 1260 N m<sup>-1</sup>.

The reactivity of  $[Mn(CO)_3(DBCat)]^-$  toward the CO substitution by bulky PPh<sub>3</sub> was studied in more detail. Besides the substitution reaction following Eq. (1), the synthesis of  $[Mn(CO)_2(PPh_3)(DBCat)]^-$  was also attempted via the 1e reduction of  $[Mn(CO)_{4-n}(PPh_3)_n(DBSQ)]$ (n=1, 2), and via the 2e oxidative addition of DBQ to  $[Mn(CO)_4(PPh_3)]^-$ . In both cases only  $[Mn(CO)_3 (DBCat)]^-$  was produced. Obviously, the formation of  $[Mn(CO)_2(PPh_3)(DBCat)]^-$  is thermodynamically unfavourable owing to both steric demands of PPh<sub>3</sub> and the bulky DBCat ligand in the fluxional [7.9] anion  $[Mn(CO)_{3^-}(DBCat)]^-$ , and electronic effects, namely the strong  $\sigma$ and, in particular,  $\pi$ -donation DBCat  $\rightarrow$  Mn, stabilising the five-coordinate geometry [9].

# 4.2. Reversible formation of the six-coordinate adducts $\{|Mn(CO)_{3}|_{n}(L)_{n}(DBCat)| \cdot L\}^{m} (n = 0, 1)$

The reversible coordination of a Lewis base L such as bulky PPh<sub>3</sub>, PCy<sub>3</sub>, or pyridine, is a characteristic property of the anion  $[Mn(CO)_3(DBCat)]^-$ , yielding the six-coordinate adducts formulated as  $\{[Mn(CO)_3(DBCat)]^+L\}^-$ . A similar interaction was observed between the dicarbonyl derivative  $[Mn(CO)_2\{P(OEt)_3\}(DBCat)]^-$  and free  $P(OEt)_3$ . With the exception of pyridine which already reversibly coordinates at ambient temperature, a lowering of the temperature is the necessary prerequisite for the shift of the equilibrium described by Eq. (4) toward the six-coordinate adducts. It is noteworthy that hard Lewis bases with O-donor atoms (THF, H<sub>2</sub>O [25], O=PPh<sub>3</sub>) do not coordinate, independently of the temperature.

 $[Mn(CO)_{3-n}(L)_n(DBCat)]^{-}+L$ 

$$\rightleftharpoons \{ [\operatorname{Mn}(\operatorname{CO})_{\lambda=n}(L)_n(\operatorname{DBCat})] \cdot L \}^{-1} \quad (n=0,1) \quad (4)$$

The IR and UV–Vis spectra (see Section 3.2.1.), and the electrochemically reversible 1e oxidation (see Section 3.2.2.) of the six-coordinate adducts closely correspond with those of the stable six-coordinate anions [Re(CO)<sub>4-n</sub>-(L)<sub>n</sub>(DBCat)]<sup>-</sup> (n = 1, 2) [26], being thus consistent with a (pseudo)octahedral arrangement of the ligands at the Mn centre. For this geometry, the  $\pi$ -donation DBCat  $\rightarrow$  Mn becomes strongly diminished and the DBCat ligand possesses a predominant  $\sigma$ -donor character [9.26]. The lowest  $\pi \rightarrow \pi^*$  electronic transition in the UV–Vis spectra of the five-coordinate anions becomes replaced by a less intense  $\pi^* \rightarrow \sigma^*$  LMCT transition characteristic for the six-coordinate anions [9.26].

The isoelectronic anions  $[M(CO)_3(Cat)]^2$  and  $[M(CO)_3$ . (DBCat)]<sup>2-</sup> (M=Cr, Mo, W) also form six-coordinate adducts with tert-phosphines, -phosphites and CO [1-3]. The temperature-dependent ability of these five-coordinate species to take up the sixth ligand was found to increase in the order  $Cr \ll Mo < W$ . This trend in the reactivity generally holds for other families of coordinatively unsaturated, formally d<sup>6</sup> transition metal complexes: (i)  $\{Mn(CO)_{3-n}\}$  $(L)_n(DBCat)$  [ (n=0, 1) studied herein, and invariably six-coordinate [Re(CO)<sub>4-n</sub>(L)<sub>n</sub>(DBCat)]<sup>-</sup> (n=0-2) [26]. (ii)  $[Mn(CO)_3(2,2'-bipyridine)]^-$  [15] and  $[Re(CO)_3 (nPrCN)_n(2,2'-bipyridine)]^-$  (n=0, 1) [11,13], and (iii)  $[M(triphos)(DBCat)]^+$  (M = Co, Rh, Ir) [21.22]. The fact that the anion  $[Mn(CO)_3(DBCat)]^-$  takes up Lewis bases more readily than the isostructural dianion  $[Cr(CO)_3]$ (DBCat)]<sup>2-</sup>, reflects the higher Lewis acidity of the Mn centre [9,17]. It is obvious that transition metals with the less diffuse 3d orbitals generally form more  $\pi$ -delocalized, more sterically hindered, and therefore less reactive complexes than are the derivatives with 4d and, in particular, 5d metals.

The reactivity of the coordinatively unsaturated complexes  $[M(CO)_{\lambda}(ChL)]^{n}$  toward the uptake of Lewis bases can also be tuned by a variation of the  $\pi$ -donor ability of the redox-active chelated ligand (ChL). For instance, the coordination of a ChL with a higher energy of its frontier orbitals, i.e. a stronger  $\pi$ -donor, usually results in a less valence-localized bonding. In addition, increased steric hindrance and donor ability of groups attached on a particular ChL may better protect the coordinative unsaturation at the metal centre. Examples are given below:

(i) The influence of electron-releasing and bulky substituents on a ChL can be documented on the couples  $[Cr(CO)_3(Cat)]^2$  and  $[Cr(CO)_3(DBCat)]^2$  where only the former dianion forms 18e adducts with  $P(OMe)_3$  at low temperatures [2,3], and  $[Re(CO)_3(bpy)] = (bpy = 2.2'-bipyridine)$  and  $[Re(CO)_3(4.4'-dimethyl-bpy)]^-$  where the enhanced  $\pi$ -donation to the Re centre in the latter anion prevents coordination of acetonitrile at ambient temperature [13].

(ii) The other possibility is the variation of ChL itself. Thus, in this work it has been shown that the anion  $[Mn(CO)_3(DBCat)]^-$  takes up reversibly a number of Lewis bases whereas the related anions  $[Mn(CO)_3(\alpha-diimine)]^-$  ( $\alpha$ -diimine = e.g. 2.2'-bipyridine or 1.4-R-1.4-diaza-1.3-butadienes) remain intact under the same conditions owing to a completely delocalized  $\pi$ -bonding in the Mn( $\alpha$ -diimine) metallacycle [15–17]. Another example is the dianion  $[Cr(CO)_3(benzene-1.2-dithiolate)]^2^-$ . This compound reacts smoothly with CO to give the 18e tetracarbonyl product [5] whereas no such reaction occurs for the related complex  $[Cr(CO)_3(DBCat)]^2^-$  containing the stronger  $\pi$ -donor DBCat ligand [3].

(iii) The last option, investigated in this work, is an attack of electrophiles at the oxygen lone pairs of the basic DBCat ligand in  $[Mn(CO)_3(DBCat)]^-$ . Such interaction largely reduces the  $\pi$ -donation from the DBCat donor toward the

Mn(CO), fragment and induces coordination of a Lewis base L which is otherwise unreactive. This phenomenon has been documented by the facile formation of the six-coordinate adducts  $[Mn(CO)_3(L)(DBCat \cdot BF_3)]^-$  (L = PPh<sub>3</sub>, THF) and  $[Mn(CO)_3(PPh_3)(DBCat \cdot CS_2)]^-$  (see Sections 3.3.1. and 3.3.2.). Consistently with the uptake of the hard Lewis base THF and fairly large  $\nu(CO)$  wavenumbers of the former two adducts, the DBCat  $\cdot$  BF<sub>3</sub> ligand electronically closely resembles the 1e-oxidized DBSQ ligand in the complexes  $[Mn(CO)_3(L)(DBSQ)]$  (L=THF, PPh<sub>3</sub>) [9.25.35]. The electron-withdrawing power of CS<sub>2</sub> relative to that of BF<sub>3</sub> is apparently lower, but still sufficient to induce coordination of a soft Lewis base such as PPh<sub>3</sub>. Interestingly, this approach was also employed for the complexes  $[M(CO)_3(Cat)]^{2-1}$  and  $[M(CO)_3(DBCat)]^{2-1}$  (M = Cr, Mo, W). In this instance, the coordination of PR<sub>3</sub>, P(OR)<sub>3</sub>, and CO was facilitated by the presence of hydrogen-bonding electrophiles such as excess catechol or methanol [1-3].

## 4.3. Mechanism of the reaction of $|Mn(CO)_{3}(DBCat)|^{-1}$ with $CS_{2}$

Like  $[Mn(CO)_5]^{-}$  [29]. also  $[Mn(CO)_3(DBCat)]^{-}$ reacts slowly with CS<sub>2</sub> and converts into the trithiocarbonate complex  $[Mn(CO)_4(S_2CS)]^-$ . The second reaction product is uncoordinated 4.6-di-tert-butyl-1.3-benzdioxol-2-thione, DBBT (see Scheme 1). The actual reaction mechanism is apparently rather complex as it involves both disproportionation of the CS<sub>2</sub> reactant as well as CO-ligand variation at the Mn centre. No intermediate carbonyl species could be isolated or spectroscopically detected at variable temperatures. The same situation applies for the anion  $|Mn(CO)_5|^{-1}$ . Its thermal reaction with  $CS_2$  has been assumed [29] to proceed via the metalladithiocarboxylate (Mn(CO)5and CO-substituted [Mn(CO)<sub>4</sub>(CS<sub>2</sub>)(SCS)]  $(\hat{\mathbf{C}}\hat{\mathbf{S}}_2)$ intermediates, yielding ultimately [Mn(CO)4(S2CS)] = and free CS. An alternative reaction path proposed involves the [Mn(CO)<sub>5</sub>S]<sup>-</sup> transient which is known to undergo insertion of CS<sub>2</sub> into the Mn-S bond [29].

The anion [Mn(CO)<sub>3</sub>(DBCat)] = probably reacts with CS<sub>2</sub> according to the mechanism presented in Scheme 1. The initial attack of CS<sub>2</sub> is anticipated to occur at the less sterically hindered oxygen atom of the DBCat ligand. The LUMO of CS2, largely localized on the electrophilic carbon atom, can overlap with the 3b<sub>1</sub> (DBCat) HOMO dominantly localized on the oxygen atoms (the lone pair of the oxygen) involved in the  $\pi$ -donation toward the Mn(CO) f fragment. This step increases the Lewis acidity of the Mn centre and weakens the Mn=O bonds. Indeed, in the presence of PPh<sub>3</sub> the reaction provides at ambient temperature the stable six-coordinate adduct { [ Mn(CO)<sub>3</sub>(DBCat·CS<sub>2</sub>) ] · PPh<sub>3</sub> ] <sup>-</sup>, which proved impossible in the absence of CS2. Coordination of PPh3 at the Mn centre then apparently inhibits the further course of the reaction with CS<sub>2</sub> as  $[Mn(CO)_4(S_2CS)]^-$  was totally absent in the reaction mixture. It is reasonable to postulate that, in the absence of  $PPh_{33}$  the coordination site available at



the Mn centre becomes occupied by a sulphur atom of the CS<sub>2</sub> attached to the DBCat ligand. Alternatively, direct coordination of a second CS<sub>2</sub> molecule may afford [Mn(CO)<sub>3\*</sub>  $(SCS)(DBCat \cdot CS_2)$  (see Scheme 1). In both possible intermediates coupling of two CS<sub>2</sub> molecules takes place which results in their disproportionation producing the trithiocarbonate ligand. The C=S fragment becomes bound to both oxygen atoms of the DBCat ligand concomitantly with the cleavage of the Mn-O bonds. The source of the fourth carbonyl ligand in the  $[Mn(CO)_4(S_2CS)]^-$  product must be either  $[Mn(CO)_3(DBCat)]^-$  itself or some other tricarbonyl transient. However, it remains unclear at which stage of the reaction course the CO-releasing step occurs, and which mechanism operates. It is noteworthy that similar COligand disproportionation has been reported for the coordinatively unsaturated radical [Mn(CO)3(DBSQ)], which led to  $[Mn(CO)_4(DBSQ)]$ .  $[Mn(DBSQ)_2]_4$  and free DB(S)Q 1251.

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#### References

- D.J. Darensbourg, K.K. Klausmeyer, B.L. Mueller and J.H. Reibenspies, Angew. Chem., Int. Ed. Engl., 31 (1992) 1503.
- [2] D.J. Darensbourg, K.K. Klausmeyer and J.H. Reibenspies, Inorg. Chem., 34 (1995) 4676.
- [3] D.J. Darensbourg, K.K. Klausmeyer and J.H. Reibenspies, Inorg. Chem., 35 (1996) 1529.
- [4] D. Sellmann, W. Ludwig, G. Huttner and L. Zsolnai, J. Organomet. Chem., 294 (1985) 199.
- [5] D. Sellmann, M. Wille and F. Knoch, Inorg. Chem., 32 (1993) 2534.
- [6] D.J. Darensbourg, K.K. Klausmeyer and J.H. Reibenspies, Inorg. Chem., 35 (1996) 1535.
- [7] F. Hartl, A. Vlček, Jr., L.A. deLearie and C.G. Pierpont, Inorg. Chem., 29 (1990) 1073.
- [8] F. Hartl and A. Vlček, Jr., Inorg. Chem., 30 (1991) 3048.
- [9] F. Hartl, D.J. Stufkens and A. Vlček, Jr., Inorg. Chem., 31 (1992) 1687.
- [10] G.J. Stor, F. Hartl, J.W.M. van Outersterp and D.J. Stutkens, Organometallics, 14 (1995) 1115.
- [11] J.W.M. van Outersterp, F. Hartl and D.J. Stufkens, Organometallics, 14 (1995) 3303.
- [12] B.D. Rossenaar, F. Hartl and D.J. Stufkens, Inorg. Chem., 35 (1996) 6194.
- [13] F.P.A. Johnson, M.W. George, F. Hartl and J.J. Turner, Organometallics, 15 (1996) 3374, and Refs. 1~13 therein.
- [14] Y.F. Lee, J.R. Kirchhoff, R.M. Berger and D. Gosztola, J. Chem. Soc., Dalton Trans., (1995) 3677.
- [15] F. Hartl, B.D. Rossenaar, G.J. Stor and D.J. Stufkens, Recl. Chim. Pays-Bays, 114 (1995) 565.
- [16] B.D. Rossenaar, F. Hartl, D.J. Stufkens, C. Amatore, E. Maisonhaute and J.-N. Verpeaux, Organometallics, in press.
- [17] F. Haril, B.D. Rossenaar, M.P. Wilms, D.J. Stufkens and E.J. Baerends, manuscript in preparation.
- [18] H.A. Nieuwenhuis, Ph.D. Thesis, University of Amsterdam, 1994.
- [19] H.T. Dieck, W. Rohde and U. Behrens, Z. Naturforsch., Teil B, 44 (1989) 158.
- [20] M.P. Aarnts, F. Hartl, K. Peelen, D.J. Stufkens, C. Amatore and J.-N. Verpeaux, Organometallics, in press.

- [21] P. Barbaro, C. Bianchini, K. Linn, A. Meli and F. Vizza, Inorg. Chim. Acta, 198–200 (1992) 31.
- [22] F. Hartl, P. Barbaro, I. Bell, R.J.H. Clark, T.L. Snoeck and A. Vlček, Jr., Inorg. Chim. Acta, 252 (1996) 157
- [23] S. Greulich, W. Kaim, A.F. Stange, H. Stoll, J. Fiedler and S. Záliš-Inorg, Chem., in press.
- [24] F. Hartl, M.P. Aarnts and K. Peelen, Coll. Czech. Chem. Commun., 61 (1996) 1342.
- [25] F. Hartl, Inorg. Chim. Acta, 232 (1995) 99.
- [26] F. Hartl and A. Vlček, Jr., Inorg. Chem., 31 (1992) 2869.
- [27] D.N. Hendrickson, Y.S. Sohn and H.B. Gray, Inorg. Chem., 10 (1971) 1559.
- [28] R.A. Faltynek and M.S. Wrighton, J. Am. Chem. Soc., 100 (1978) 2701.
- [29] I.B. Benson, J. Hunt, S.A.R. Knox and V. Oliphant, J. Chem. Soc., Dalton Trans., (1978) 1240.
- [30] M. Krejčík, M. Daněk and F. Hartl, J. Electroanal. Chem. Interfacial Electrochem., 317 (1991) 179.
- [31] G. Gritzner and J. Kuta, Pure Appl. Chem., 56 (1984) 461.
- [32] P.S. Braterman, in Metal Carbonyl Spectra, Academic Press, London, 1975, p. 36.
- [33] C.A. Tolman, Chem. Rev., 77 (1977) 313.
- [34] G. Ferguson, P.J. Roberts, E.C. Alyea and M. Khan, Inorg. Chem., 17 (1978) 2965.
- [35] F. Hartl and A. Vlček, Jr., Inorg. Chem., 35 (1996) 1257.
- [36] A.J. Bard and L.R. Faulkner, in Electrochemical Methods: Fundamentals and Applications, Wiley, New York, 1980, pp. 215– 231.
- [37] T. van der Graaf, D.J. Stufkens, J. Víchová and A. Vlček, Jr., J. Organomet, Chem., 401 (1991) 305.
- [38] H.S. Booth and D.R. Martin, in Boron Trifluoride and its Derivatives, Wiley, New York, 1949.
- [39] D.F. Shriver and J. Posner, J. Am. Chem. Soc., 88 (1966) 1672.
- [40] W.A. Schenk, D. Kuemmerle and T. Schwietzke, J. Organomet. Chem., 349 (1988) 163.
- [41] C. Bianchini, C. Mealli, A. M. Ii and G. Scapacci, J. Chem. Soc., Dalton Trans., (1982) 799.
- [42] M. Torres, A. Clement and O.P. Strausz, J. Org. Chem., 45 (1980) 2271.
- [43] P. de Mayo, A.C. Weedon and G.S.K. Wong, J. Org. Chem., 44 (1979) 1977.
- [44] E. Gruendemann, O. Martin and A. Wenzel, Org. Magn. Resonance, 12 (1979) 95.
- 1451 W. Autenrieth and H. Hefner, Chem. Ber., 38 (1925) 2151
- [46] C.A. Streuli, Anal. Chem., 32 (1960) 985.
- [47] G.T. Palmer, F. Basolo, L.B. Kool and M.D. Rausch, J. Am. Chem. Soc., 108 (1986) 4417.