

# Selenium-77 NMR studies of cyclopentadienylchromium selenium species

## Evidence of conformers

Philip A.W. Dean <sup>a,\*</sup>, Lai Yoong Goh <sup>b,1</sup>, Ian D. Gay <sup>c</sup>, R.D. Sharma <sup>c</sup>

<sup>a</sup> Department of Chemistry, University of Western Ontario, London, Ont. N6A 5B67, Canada

<sup>b</sup> Department of Chemistry, University of Malaysia, 59100 Kuala Lumpur, Malaysia

<sup>c</sup> Department of Chemistry, Simon Fraser University, Burnaby, B.C. V5A 1S6, Canada

Received 8 April 1996; revised 10 October 1996

### Abstract

Variable-temperature <sup>77</sup>Se NMR spectroscopic studies of the complexes [CpCr(CO)<sub>2</sub>]<sub>2</sub>Se (1) and [CpCr(CO)<sub>2</sub>]<sub>2</sub>Se<sub>2</sub> (2) have been carried out. A singlet <sup>77</sup>Se resonance is found for 1 at 213–296 K, but the broadness at the higher temperatures suggests the existence of rotamers exchanging at an intermediate rate on the time scale of Δδ<sub>Se</sub>. For 2, the observations point to the existence of two conformers over the range 213–330 K, with relative proportions varying from ca. 1:3.4 at 320 K to ca. 1:6.4 at 213 K. This conclusion is supported by <sup>13</sup>C NMR spectra at 213 and 298 K. Also reported are <sup>77</sup>Se NMR data for Cp<sub>2</sub>Cr<sub>2</sub>(CO)<sub>3</sub>Se<sub>2</sub> (3), produced in situ by thermolysis of 2 in solution, and solid-state CP-MAS <sup>13</sup>C and <sup>77</sup>Se NMR data for [CpCrSe]<sub>4</sub> (4).

**Keywords:** Chromium; Selenium; NMR; Cyclopentadienyl; Carbon-13; Conformers

### 1. Introduction

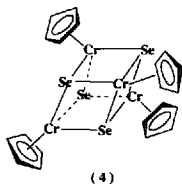
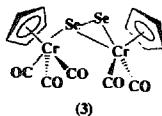
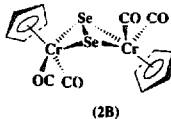
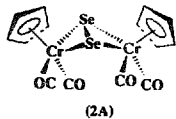
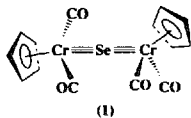
There now exists an extensive range of transition metal organometallic complexes containing selenide and polyselenide ligands [1,2]. However, compared with the situation for organoselenium compounds (e.g. Refs. [3,4]), the use of <sup>77</sup>Se NMR for their characterization and further study has been infrequent (e.g. Ref. [1]). Of

the bonding modes that occur in these organometallic species, those that have been subjected to the <sup>77</sup>Se NMR probe include: η<sup>2</sup>-Se<sub>2</sub><sup>2-</sup>, *n* ≥ 4 [5–8] (and -Se<sub>n</sub>S<sub>2</sub><sup>2-</sup> [9]); bent μ<sub>2</sub>-Se<sup>2-</sup> [10,11], μ<sub>2</sub>-η<sup>2</sup>-Se<sub>2</sub><sup>2-</sup> [5]; μ<sub>2</sub>-η<sup>4</sup>-tetradentate bridging Se<sub>4</sub><sup>2-</sup> [11].

In this paper, we report variable-temperature <sup>77</sup>Se and <sup>13</sup>C NMR spectral data for [CpCr(CO)<sub>2</sub>]<sub>2</sub>Se (1) and [CpCr(CO)<sub>2</sub>]<sub>2</sub>Se<sub>2</sub> (2) [12,13], which provide evidence for the existence of conformers in solution. To provide a more complete set of data for Se-containing organometallic compounds of chromium, we have also measured the <sup>77</sup>Se NMR spectra of Cp<sub>2</sub>Cr<sub>2</sub>(CO)<sub>3</sub>Se<sub>2</sub> (3) [13] and Cp<sub>4</sub>Cr<sub>4</sub>Se<sub>4</sub> (4) [14], the latter in the solid state.

\* Corresponding author. Office tel.: (+1) 519 679 2111 ext. 6331; dept. fax: (+1) 519 661 3022; e-mail: pawdean@julian.uwo.ca.

<sup>1</sup> Present address: Department of Chemistry, Monash University, Clayton, Vic. 3168, Australia.



## 2. Experimental

The complexes 1, 2 and 4 were prepared from  $[\text{CpCr}(\text{CO})_3]_2$  as previously reported [12–14]. Toluene was dried over 3A molecular sieves.

All samples for solution NMR were prepared in 10 mm tubes under argon in a glove bag, and all solution NMR spectra were obtained at UWO. Carbon-13 NMR spectra of 0.05 M solutions of 1 and 2 were measured on both Varian Gemini-200 and Varian XL-300 spectrometer systems, at 50.30 and 75.42 MHz, and the  $^{77}\text{Se}$  NMR spectra of the same solutions were accumulated using the XL-300 system operating at 57.20 MHz. In all cases the magnetic field was pre-shimmed, then the spectra were measured without a lock. (Field drift was negligible.) Probe temperatures were measured using a calibrated thermocouple probe in a stationary sample of toluene. Solution NMR scans were obtained in the range 213–330 K, with the temperature variation as indicated in Table 1. The reference for  $^{13}\text{C}$  was the  $\text{PhCH}_3$  signal of the solvent ( $\delta_{\text{C}}$  (relative to internal TMS) = 21.37 (297 K), 21.44 (213 K), 21.47 (183 K)). For  $^{77}\text{Se}$ , external referencing was by sample interchange with  $\text{Me}_2\text{Se}$  at ambient probe temperature. The transverse  $^{77}\text{Se}$  relaxation time of 2 in toluene solution was measured using the inversion–recovery method. Typically, solution-state  $^{77}\text{Se}$  NMR spectra were recorded using a spectral window of 20 kHz,

Table 1  
Variable-temperature  $^{13}\text{C}$  and  $^{77}\text{Se}$  NMR data for some cyclopentadienylchromium selenides

Compound	Temperature /K	$\delta_{\text{Se}}^a$ ( $\Delta\nu_{1/2}$ (approx)/Hz)	$\delta_{\text{C}}^b$ ( $\Delta\nu_{1/2}$ (approx)/Hz)
$[\text{CpCr}(\text{CO})_2]_2\text{Se}$ (1)	213	2572.3 (60)	88.7 <sup>c</sup>
	286	2568 (720)	
	296	~2574 (1400)	88.8 <sup>c</sup>
$[\text{CpCr}(\text{CO})_2]_2\text{Se}_2$ (2)	213	-144.7 (75), -263.7 (80) <sup>d,e</sup>	91.2 <sup>f,g</sup> , 91.3 <sup>f,g</sup> , 90.5 <sup>d,f,g</sup>
	298	-136.6 (30), -259.6 (15) <sup>d,h,i</sup>	91.6 (70) <sup>j</sup> , 90.8 (6) <sup>d,j</sup>
	309	-135.3 (65), -258.7 (30) <sup>d,k</sup>	
	320	-134 (160), -258.1 (70) <sup>d,l</sup>	
	330	-258 <sup>m</sup>	
$\text{Cp}_2\text{Cr}_2(\text{CO})_2\text{Se}_2$ (3)	296	122.1 (90) <sup>n</sup> , 23.4 (60) <sup>n</sup>	93.1 <sup>c</sup> , 90.1 <sup>c</sup>
$[\text{CpCrSe}]_4$ (4) <sup>o</sup>	ca. 303	1079 <sup>p</sup> , 1018 <sup>p</sup>	90.8

<sup>a</sup> Relative to external  $\text{Me}_2\text{Se}$  at ambient probe temperature.

<sup>b</sup> Cyclopentadienyl region only. Relative to internal  $\text{SiMe}_4$ . (Primary reference  $\text{PhCH}_3$ ).

<sup>c</sup> Carbon-13 NMR data have been reported in [13]. The data presented here are consistent with the earlier data.

<sup>d</sup> Major signal.

<sup>e</sup> Intensity ratio ca. 1:6.4.

<sup>f</sup> See Fig. 1(b).

<sup>g</sup> Intensity ratio  $I(91.2):I(91.3):I(90.5) \approx 1:1:14$ .

<sup>h</sup> Intensity ratio ca. 1:3.7.

<sup>i</sup>  $T_1 = 0.42 \pm 0.02$  s.

<sup>j</sup> See Fig. 1(a).

<sup>k</sup> Intensity ratio ca. 1:3.6.

<sup>l</sup> Intensity ratio ca. 1:3.4.

<sup>m</sup> The higher frequency signal could not be observed with certainty (very broad).

<sup>n</sup> In a mixture produced by thermolysis of 2 in toluene. Intensity ratio ca. 1:1. See Fig. 2.

<sup>o</sup> CP-MAS spectra of solid 4.

<sup>p</sup> See Fig. 3.

pulsewidth of 16  $\mu$ s (tip angle ca. 80°) and an acquisition and recycle time of 0.75 s.

The solid state  $^{13}\text{C}$  and  $^{77}\text{Se}$  NMR spectra of **4** at ambient probe temperature were measured at SFU at frequencies of 37.55 and 28.51 MHz, using a home-built spectrometer with a field of 3.5 T. The general procedure and analysis of results was as described previously [15]. Hartmann–Hahn cross-polarization was achieved using matched r.f. fields of 41 and 40 kHz for  $^{13}\text{C}$  and  $^{77}\text{Se}$ . The contact times were 2 and 4 ms and the spinning rates were 2.0 and 2.5–2.9 kHz. For the CP-MAS  $^{77}\text{Se}$  NMR, the recycle time was 1 s and 65 000 transients were collected.

### 3. Results and discussion

In a VT  $^{77}\text{Se}$  NMR spectral study of **1** (Table 1), the spectrum at 296 K shows an extremely broad signal ( $\Delta\nu_{1/2}$  ca. 1400 Hz) at  $\delta_{\text{Se}} \sim 2574$ . This signal sharpens at 213 K to  $\Delta\nu_{1/2}$  60 Hz, with  $\delta_{\text{Se}} = 2572.3$ . Thus no evidence was found for a second species in the 213 K spectrum; from the signal:noise obtained, any such species must have been < 1% of the main signal (assuming the same  $\Delta\nu_{1/2}$ ). Nevertheless, the most plausible explanation for the broad signal found at 296 K is the occurrence at this temperature of two conformers, e.g. the anti- and gauche-conformers discussed below, that are undergoing exchange at an intermediate rate. The VT  $^{13}\text{C}$  NMR spectra of **1** (Table 1) provide no evidence for an exchange process, but such a process may well be rapid on the time scale of  $\Delta\nu_{\text{C}}$  under all temperature conditions used. The  $^{13}\text{C}$  spectra of **1** measured here are consistent with earlier ambient temperature  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of  $[\text{CpCr}(\text{CO})_2]_2\text{E}$  (E = S, Se), which showed magnetically equivalent Cp rings and CO ligands in the molecules on the time scale of  $\Delta\nu_{\text{H}}$  and  $\Delta\nu_{\text{C}}$  in the experiments [13,16,17]. From the variation of  $\Delta\nu_{1/2}$  ( $^{77}\text{Se}$ ) with temperature,  $\Delta H^\ddagger \approx 17\text{--}29 \text{ kJ mol}^{-1}$  for rotation about the  $\text{Cr}=\text{Se}=\text{Cr}$  axis of  $[\text{CpCr}(\text{CO})_2]_2\text{Se}$ , for assumed viscosity broadenings of 0–50 Hz for the signal at 213 K.

We note that two different forms of  $[\text{CpCr}(\text{CO})_2]_2\text{Se}$ , thought to be rotamers, can be isolated by fractional crystallization, though they equilibrate rapidly on the preparative time scale in solution [18]. The latter observation suggests ready rotation about  $\text{Cr}=\text{Se}=\text{Cr}$ , consistent with our results. Nonempirical molecular orbital calculations [19] show virtually no electronic barrier to intramolecular rotation about the  $\text{Cr}=\text{S}=\text{Cr}$  axis of  $[\text{CpCr}(\text{CO})_2]_2\text{S}$  (for which rotation about the  $\text{Cr}=\text{S}=\text{Cr}$  bond is rapid on the time scales of  $\Delta\nu_{\text{H}}$  and  $\Delta\nu_{\text{C}}$  [16]). Thus the sum of eigenvalues (energies) of the occupied molecular orbitals was found to be identical for both the anti- and gauche-conformations.

The highly deshielded  $^{77}\text{Se}$  resonance of **1** places it close to the high frequency limit of the range observed for  $^{77}\text{Se}$  [3–5]. Most probably this extreme deshielding derives from the involvement of the  $\pi$ -electrons of Se in the unusual cumulated  $\text{Cr}=\text{Se}=\text{Cr}$  linkage [3,4].

VT  $^{13}\text{C}$  and  $^{77}\text{Se}$  NMR spectral characteristics of a solution of **2** in toluene (Table 1) are consistent with the existence of two conformers with a molar ratio of ca. 1:3.4 (at 320 K) to 1:6.4 (at 213 K). The predominant conformer possesses  $\delta_{\text{Se}}$  ranging from  $-263.7$  (213 K) to  $-258$  (330 K), with corresponding peak half-widths ranging from 80 Hz to 175 Hz, with a minimum (15 Hz) at 298 K. For this resonance,  $T_1 = 0.42 \pm 0.02$  s at 298 K. Such a value is at the lower end of  $^{77}\text{Se}$  longitudinal relaxation times that have been reported [3,4]. The less abundant conformer possesses  $\delta_{\text{Se}}$  at higher frequency, ranging from  $-144.7$  ( $\Delta\nu_{1/2} = 75$  Hz) at 213 K to  $-134$  ( $\Delta\nu_{1/2} = 160$  Hz) at 320 K; at 330 K the peak is too broad for observation. Evidently interconversion of the two conformers occurs at an increasing rate as the temperature is raised. From the linewidth variation of the two isomers in the range 298–330 K,  $\Delta H^\ddagger \approx 58 \text{ kJ mol}^{-1}$  (assuming the no-exchange values of  $\Delta\nu_{1/2}$  are negligible).

The indication from the  $^{77}\text{Se}$  NMR spectra that two conformers of **2** occur is consistent with  $^{13}\text{C}$  NMR spectroscopic observations, which are illustrated in Fig.

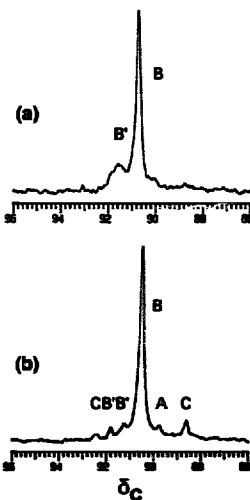


Fig. 1. The cyclopentadienyl region of the 50.30 MHz  $^{13}\text{C}$  NMR spectrum of  $[\text{CpCr}(\text{CO})_2]_2\text{Se}_2$  (**2**) at (a) 298 K, (b) 213 K. A =  $[\text{CpCr}(\text{CO})_2]_2\text{Se}$  (**1**), B/B' =  $2\text{A}/2\text{B}$ , C =  $[\text{Cp}_2\text{Cr}_2(\text{CO})_4\text{Se}_2]$  (**3**).

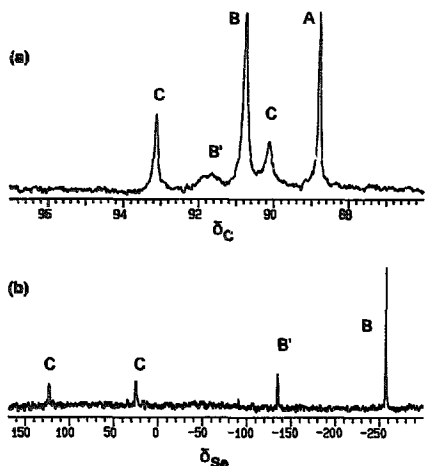


Fig. 2. (a) The cyclopentadienyl region of the 75.42 MHz  $^{13}\text{C}$  NMR spectrum at 296 K of a solution of  $[\text{CpCr}(\text{CO})_2]_2\text{Se}_2$  (2) in toluene, after heating to 330 K. (b) The 57.20 MHz  $^{77}\text{Se}$  NMR spectrum at 296 K of the same solution. (The resonance of  $[\text{CpCr}(\text{CO})_2]_2\text{Se}$  (1) could not be observed at 296 K.) Labelling in (a) and (b), A = 1, B/B' = 2A/2B, C =  $[\text{Cp}_2\text{Cr}_2(\text{CO})_2\text{Se}_2]$  (3).

1(a) and Fig. 1(b) for 298 K and 213 K. In Fig. 1(a) are shown the Cp resonances B,  $\delta_{\text{C}}$  90.8 ( $\Delta\nu_{1/2} \sim 6$  Hz)) and B' ( $\delta_{\text{C}}$  91.6 ( $\Delta\nu_{1/2} \sim 70$  Hz)) for the two conformers. On changing to 213 K (Fig. 1(b)), resonance B only

shifts slightly (to  $\delta_{\text{C}}$  90.5). However, the broad resonance B' is reduced in overall intensity relative to A (consistent with the diminution in the minor:major ratio observed in the  $^{77}\text{Se}$  NMR spectra as the temperature is reduced (see Table 1)) and resolved into two sharp lines ( $\delta_{\text{C}}$  91.2 and 91.3, each ca. 1/14 of the major signal B). This result suggests that the resonances labelled B' are those of a frozen-out structure containing two magnetically inequivalent Cp rings. We suggest that the major and minor conformers of  $[\text{CpCr}(\text{CO})_2]_2\text{Se}$  are 2A and 2B, with magnetically equivalent and inequivalent Cp rings respectively. (Fig. 1(b) also shows weak signals from 1 (labelled A) and 3 (labelled C). Based on previous demonstrations of the extraordinary ease of inter-transformations of the complexes 1–3 [13], the formation of 1 and 3 in a solution of 2 is not surprising.)

Earlier authors [13] appear to have overlooked the broad resonance B' in the  $^{13}\text{C}$  NMR spectrum of 2 at ambient temperature. Both  $^{13}\text{C}$  and  $^1\text{H}$  spectra of the complex were interpreted [13] as showing that it, like the sulfur analogue [20], possessed magnetically equivalent Cp rings and CO ligands at ambient temperature.

The  $^{77}\text{Se}$  NMR signals (Table 1) of the  $\mu, \eta^2\text{-}\eta^2\text{-Se}_2$  group in the conformers of 2, -137 and -260 ppm at 298 K, are more shielded than those observed for  $\mu_2\text{-}\eta^2\text{-Se}_2$  groups in either organic diselenides,  $\text{R}_2\text{Se}_2$  ( $\delta_{\text{Se}}$   $\sim$  110–550 [3]) or  $[(\text{Pr}^i\text{Cp})_2\text{Ti}]_2\text{Se}_2$  ( $\delta_{\text{Se}}$  = 1412 [5]).

The ambient-temperature  $^{13}\text{C}$  and  $^{77}\text{Se}$  NMR spectra of a solution of 2 after heating to 330 K (Fig. 2(a) and Fig. 2(b)) show signals of 1 and 2, and also of 3, identified through its  $^{13}\text{C}$  NMR spectrum [13]. In Fig. 2, the signals of 1, 2 and 3 are labelled A,B/B' and C. We

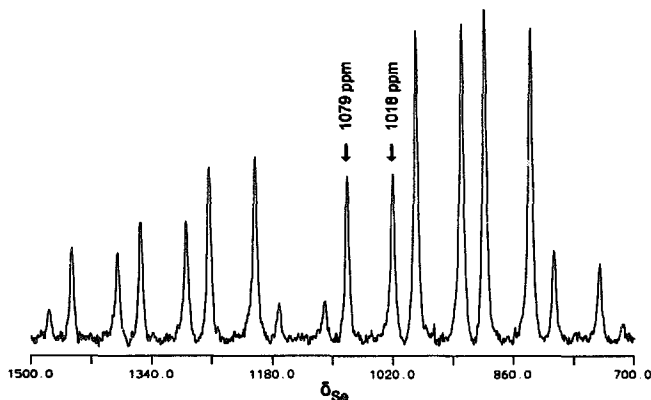


Fig. 3. The 28.51 MHz  $^{77}\text{Se}$  CP-MAS NMR spectrum of solid  $[\text{CpCrSe}]$ , (4) at ambient probe temperature and a spinning rate of 2600 Hz. The isotropic chemical shifts, indicated by the arrows, were confirmed using spinning rates from 2.5–2.9 kHz.

note again that the formation of **1** and **3** from **2** is not unexpected. Since **3** is known to be now present from the  $^{13}\text{C}$  NMR spectrum, the two new approximately equally intense resonances observed in the  $^{77}\text{Se}$  NMR spectrum can be assigned to this species,  $\delta_{\text{Se}}$  122.1 ( $\Delta\nu_{1/2} \sim 90$  Hz) and 23.4 ( $\Delta\nu_{1/2} \sim 60$  Hz). We were unable to assign these resonances further. Their separation is remarkably small for the two differently bonded atoms of a  $\mu, \eta^1: \eta^2\text{-Se}_2^{2-}$  ligand, less than  $\Delta\delta_{\text{Se}}$  observed for the two conformers of **2**, in which the bonding mode to the two chromium centres is, presumably, identical.

Compound **4** is insufficiently soluble for a solution study by either  $^{13}\text{C}$  or  $^{77}\text{Se}$  NMR. Therefore solid-state NMR spectra of **4** were obtained at ambient temperature by the CP-MAS technique. The results are included in Table 1, and the CP-MAS  $^{77}\text{Se}$  NMR spectrum is shown in Fig. 3. The  $^{13}\text{C}$  NMR spectrum shows a single Cp resonance with an unexceptional chemical shift. The solid-state  $^{77}\text{Se}$  NMR spectrum reveals two approximately axially symmetric resonances, with isotropic chemical shifts  $\delta_{\text{Se}} = 1018$  and 1079 (both  $\pm 1$  ppm). The approximate axial symmetry is consistent with a cubane structure for  $[\text{CpCrSe}_4]$ , but in the absence of crystal structure data it is not clear whether the two shifts represent different  $[\text{CpCrSe}_4]$  molecules or different Se environments within a single distorted  $[\text{CpCrSe}_4]$  molecule. Both  $^{77}\text{Se}$  resonances are less shielded by 700–800 ppm than those observed for  $\text{R}_3\text{Se}^+$  [3,4].

#### Acknowledgements

Support to LYG from the University of Malaya and Malaysian IRPA R&D Grant No. 04-07-04-211 and to PAWD as an Individual Research Grant from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

#### References

- [1] M.A. Ansari and J.A. Ibers, *Coord. Chem. Rev.*, **100** (1990) 223.
- [2] L.C. Roof and J.W. Kolis, *Chem. Rev.*, **93** (1993) 1037.
- [3] N.P. Luthra and J.D. Odom, in S. Patai and Z. Rappaport (eds.), *The Chemistry of Organic Selenium and Tellurium Compounds*, Wiley, New York, 1986, p. 189.
- [4] H.C.E. McFarlane and W. McFarlane, in J. Mason (ed.), *Multinuclear NMR*, Plenum, New York, 1987, p. 421.
- [5] D.M. Giolando, M. Papavassiliou, J. Pickardt, T.B. Rauchfuss and R. Stendel, *Inorg. Chem.*, **27** (1988) 2596.
- [6] P. Pekonen, Y. Hiltunen and R.S. Laitinen, *Acta Chem. Scand.*, **43** (1989) 914.
- [7] M. Draganjac, S. Dhingra, S.-P. Huang and M.G. Kanatzidis, *Inorg. Chem.*, **29** (1990) 590.
- [8] J.M. Cusick, *Ph.D. Thesis*, University of New South Wales, 1993.
- [9] P. Pekonen, Y. Hiltunen, R.S. Laitinen and J. Valkonen, *Inorg. Chem.*, **30** (1991) 1874.
- [10] P. Granger, B. Gautheron, G. Tausturier and S. Pouly, *Org. Magn. Reson.*, **22** (1984) 701.
- [11] H. Brunner, W. Meier, B. Huber, J. Wachter and M.L. Ziegler, *Angew. Chem. Int. Edn. Engl.*, **25** (1986) 907.
- [12] L.Y. Goh, C. Wei and E. Sinn, *J. Chem. Soc. Chem. Commun.*, (1985) 462.
- [13] W. Chen, L.Y. Goh and E. Sinn, *Organometallics*, **7** (1988) 2020.
- [14] L.Y. Goh and T.C.W. Mak, *J. Organomet. Chem.*, **363** (1989) 77.
- [15] I.D. Gay, C.W.H. Jones and R.D. Sharma, *J. Magn. Reson.*, **84** (1989) 501. R.J. Batchelor, F.W.B. Einstein, L.D. Gay, C.H.W. Jones and R.D. Sharma, *Inorg. Chem.*, **32** (1993) 4378.
- [16] T.J. Greenhough, B.W.S. Kolthammer, P. Legzdins and J. Trotter, *Inorg. Chem.*, **18** (1979) 3543.
- [17] L.Y. Goh, T.W. Hambley and G.B. Robertson, *J. Chem. Soc. Chem. Commun.*, (1983) 1458.
- [18] W.A. Herrmann, J. Rohrmann and A. Schafer, *J. Organomet. Chem.*, **265** (1984) C1. W.A. Herrmann, J. Rohrmann, H. Noth, Ch.K. Narula, I. Bernal and M. Draux, *J. Organomet. Chem.*, **284** (1985) 189.
- [19] N.M. Kostic and R.F. Fenske, *J. Organomet. Chem.*, **233** (1982) 337.
- [20] L.Y. Goh, T.W. Hambley and G.B. Robertson, *Organometallics*, **6** (1987) 1051.