SYNTHESIS AND CHARACTERIZATION OF HALOGEN AND PSEUDOHALOGEN DERIVATIVES OF SUBSTITUTED VANADOCENES

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Summary

The complexes $\eta\text{-}Cp_2^{\star}V$ ($Cp^{\star} = \eta\text{-}C_5H_4Me$, $\eta\text{-}C_5HMe_4$, $\eta\text{-}C_5Me_5$) react with PX_3 ($X = Cl$, Br, I) to give the dihalogenated derivatives $\eta\text{-}Cp_2^{\star}VX_2$. The complexes $\eta\text{-}Cp_2^{\star}VIX$ ($X = Cl$, Br) and $\eta\text{-}Cp_2^{\star}V(NCS)_2$ are obtained by the oxidative addition of IX ($X = Cl$, Br) and $(SCN)_2$ to the corresponding substituted vanadocene. All the products have been characterized by IR and EPR spectroscopy. The EPR spectra of the complexes have been recorded in solution at room temperature and in glasses, and the g values and solution coupling constants are discussed. The unpaired electron is in an orbital of A_1 symmetry. The influence of the ring methyl substituents is discussed.

Introduction

There is an increasing interest in the chemistry of the peralkylated metallic cyclopentadienyls because of the differences between their structures and reactivities and those of their unsubstituted analogues [1,2]. The higher electron donor ability of the $C_5Me_5^-$ compared with the analogous $C_5H_5^-$ ligand plays an important role in the stabilization of low oxidation states of the metal and influences the stability of the metal–ligand bond in complexes of the type $(\eta\text{-}Cp^{\star})_2ML_n$. Such electron donation becomes apparent in a stronger ligand field in the case of the decamethylmetallocenes [3]. At the same time the steric bulk of the $C_5Me_5^-$ ligands also affects the reactivity of its metallic complexes, and can stabilize reaction intermediates [4]. Some of the chemistry of decamethylvanadocene has been described recently [5,6].

We describe here the synthesis and characterization of the complexes $Cp_2^{\star}VXY$ (X,Y are halogens), and the corresponding dithiocyanogen derivatives $Cp_2^{\star}V(NCS)_2$, by use of a known method which can give high yields of halogen derivatives [7].

Results and discussion

When ethereal solutions of Cp_2^*V and PX_3 (X = Cl, Br, I) are mixed there is in all cases immediate precipitation of brown or green solids which have been identified as η-$Cp_2^*VX_2$ (X = Cl, Br, I). The halogen mixed derivatives η-Cp_2^*VXY (X = I, Y = Cl, Br) can be obtained similarly by addition of IBr or ICl to the ethereal solutions of the corresponding dicyclopentadienylvanadium.

Low temperature reactions between solutions of η-Cp_2^*V and $(SCN)_2$ give precipitates of the corresponding dithiocyanogen derivatives η-$Cp_2^*V(NCS)_2$.

All the products are air stable. Their solubilities in polar solvents depend very much on the ligands X and Y and on the ring substituents. There is an increase in the solubility on going from Cl to I and also as expected when the number of methyl groups in the ring is increased.

The IR spectra of the products show the characteristic bands of the η-MeCp rings at 3100–2900 m, 1500–1430 m, 1300–1250 m, 1040 m, 860–830 s cm^{-1} [8], and also for η-Me_4Cp and η-Me_5Cp at 2990–2930 m, 2760 m, 1480–1380 m, 1060 w, 1020 w, 740–720 w [3]. Furthermore there are bands of medium intensity at 440–400, 380–350 and 300–280 cm^{-1} which can be tentatively assigned to metal–ring vibrations, although bending modes of the methyl groups also appear in this range. The bands from the metal–halide vibrations appear in the range 300–80 cm^{-1}, and can be assigned (see Table 1) by taking account of the fact that there must be strong bands which are shifted to lower frequencies in the order Cl > Br > I. Thus the band in the range 250–230 cm^{-1} is assigned to ν_a(VCl). Since ν(MBr)/ν(MCl) 0.75 for tetra- and hexa-coordinate complexes [9], the bands at 170–160 cm^{-1} can be assigned to ν_a(VBr). The bands corresponding to ν(VI) are at 130–120 cm^{-1} in agreement with the relationship ν(MI)/ν(MBr) 0.83 [9].

The characteristic bands of the NCS ligands are listed in Table 2. The frequencies of these bands indicate that in all cases the thiocyanate ligand is coordinated through the nitrogen atom [10]. This is confirmed by the measurement of the

TABLE 1

IR BANDS (cm^{-1}) FROM METAL–HALOGEN BONDS

Compounds	ν(VCl)	ν(VBr)	ν(VI)
$(MeCp)_2VCl_2$	246 s, 210 s		
$(MeCp)_2VBr_2$		163 s, 150 s	
$(MeCp)_2VI_2$			134 s, 120 s
$(MeCp)_2VIBr$		165 s	136 s
$(MeCp)_2VICl$	242 s		136 s
$(Me_4Cp)VCl_2$	243 s, 214 s		
$(Me_4Cp)_2VBr_2$		165 s, 152 s	
$(Me_4Cp)_2VI_2$			134 s, 120 s
$(Me_4Cp)_2VIBr$		167 s	135 s
$(Me_4Cp)_2VICl$	244 s		136 s
$(Me_5Cp)_2VCl_2$	240 s, 200s		
$(Me_5Cp)_2VBr_2$		165 s, 150 s	
$(Me_5Cp)_2VI_2$			134 s, 118 s
$(Me_5Cp)_2VIBr$		168 s	137 s
$(Me_5Cp)_2VICl$	245 s		136 s

TABLE 2

IR BANDS (cm^{-1}) FOR SCN LIGANDS

Complexes	ν(CN)		δ(NCS)
	Nujol ^{a}	CH$_2$Cl$_2$ solution	
(MeCp)$_2$V(NCS)$_2$	2090(2.6)	2090	485, 472
	2071(2.3)	2070	
	2030 sh		
(Me$_4$Cp)$_2$V(NCS)$_2$	2090(2.5)	2090	483, 470
	2069(2.4)	2065	
	2027 sh		
(Me$_5$Cp)$_2$V(NCS)$_2$	2093(2.5)	2092	480, 473
	2069(2.3)	2069	
	2033 sh		

^{a} The value of the internal standard ratio is shown in parentheses. ν(CS) obscured by cyclopentadienyl absorption.

internal standard ratio of the band corresponding to ν(CN) in the solid, using salicyclic acid as a model [11]. Each of the thiocyanate complexes contains two ligands NCS which give rise to different vibration modes. These modes may be in phase or out of phase, thus giving rise to the appearance of two separate bands corresponding to ν(CN). In Nujol, the IR spectrum shows a shoulder at 2030 cm^{-1}, which is probably due to solid state effects since it is absent when the spectrum is recorded for solutions in CH$_2$Cl$_2$.

The EPR spectra of the complexes in chloroform at room temperature show the eight lines expected for the hyperfine interaction of the unpaired electron with the ^{51}V nucleus (99.8% abundance, $I = 7/2$). No superhyperfine coupling with the halogen or nitrogen ligands was detected. These spectra can be interpreted by use of the spin Hamiltonian: $\hat{H} = \langle g_{iso} \rangle \beta H.\hat{S}_z + \langle A_{iso} \rangle I_z \hat{S}_z$. The g_{iso} and A_{iso} values determined after applying the second order correction [12] are listed in Table 3. There is satisfactory agreement between the values of these parameters for our compounds and those for a large number of vanadium(IV) complexes of similar symmetry [13].

The g_{iso} values for all the complexes are close to that for free spin, indicating considerable delocalization of the unpaired electron over the ligands. This delocalization is shown also by the decrease found in the values of A_{iso} going from Cp$_2^*$VCl$_2$ to Cp$_2^*$VI$_2$. A slight decrease in the values of A_{iso} can be observed (see Table 3) as the number of methyl groups on the cyclopentadienyl ring is increased, and this could be a consequence of the electron releasing inductive effect of these groups, which could increase the electronic delocalization; similar effects were observed for some niobium(IV) cyclopentadienyls [14].

Figure 1 shows the linear plot of A_{iso} against g_{iso} for the $(\eta$-Me$_5$Cp)$_2$VCL$_2$ complexes; at least two factors must be operating, one of them the delocalization between the ligands and the other the degree of covalent character of the V–X bonds. Thus as the degree of covalent character falls in the sequence Cp$_2^*$VI$_2$ > Cp$_2^*$VIBr > Cp$_2^*$VICl > Cp$_2^*$VBr$_2$ > Cp$_2^*$V(NCS)$_2$ > Cp$_2^*$VCl$_2$, A_{iso} decreases and g_{iso} increases, because of corresponding decrease in the spin-orbit coupling.

TABLE 3

EPR PARAMETERS FOR THE COMPLEXES Cp_2^*VXY ^{a} (the hyperfine coupling $-K$ and P are in units of 10^4 cm^{-1})

Complex	A_{iso}	g_{iso}	g_x	g_y	g_z	A_x	A_y	A_z	a^2	b^2	$-K$	P	χ	r^{-3}	λ
$(MeCp)_2VCl_2$	68.7	1.986	1.980	1.969	2.000	74	116	18	0.96	0.04	74	106	−2.21	2.26	130
$(MeCp)_2VBr_2$	63	2.004	1.991	1.988	2.000	67	101	21	0.96	0.04	68	90	−2.03	1.92	102
$(MeCp)_2VI_2$	56	2.026	1.998	1.990	2.000	59	88	19	0.96	0.04	61	80	−1.82	1.71	85
$(MeCp)_2VIBr$	59	2.017	1.994	1.989	2.000	62	94	18	0.96	0.04	63	86	−1.88	1.83	92
$(MeCp)_2VICl$	62	2.006	1.987	1.978	2.000	66	99	18	0.96	0.04	66	90	−1.88	1.92	100
$(MeCp)_2V(NCS)_2$	67	1.991	1.987	1.958	2.000	70	112	18	0.96	0.04	71	105	−2.12	2.24	110
$(Me_4Cp)_2VCl_2$	67	1.987	1.985	1.972	2.000	72	106	17	0.97	0.03	70	97	−2.09	2.07	115
$(Me_4Cp)_2VBr_2$	60	2.003	1.993	1.988	2.000	65	93	18	0.97	0.03	64	86	−1.91	1.83	90
$(Me_4Cp)_2VI_2$	54	2.002	1.999	1.989	2.000	57	87	19	0.96	0.04	60	79	−1.79	1.68	80
$(Me_4Cp)_2VIBr$	57	2.019	1.997	1.988	2.000	57	90	18	0.95	0.05	60	82	−1.79	1.75	85
$(Me_4Cp)_2VICl$	59	2.008	1.996	1.987	2.000	62	89	18	0.97	0.03	62	82	−1.85	1.75	85
$(Me_4Cp)_2V(NCS)_2$	65	1.993	1.990	1.972	2.000	66	103	19	0.96	0.04	67	91	−2.00	1.94	105
$(Me_5Cp)_2VCl_2$	65	1.987	1.987	1.974	2.000	70	105	17	0.96	0.03	68	96	−2.03	2.05	110
$(Me_5Cp)_2VBr_2$	59	2.007	1.994	1.987	2.000	63	93	18	0.96	0.03	64	86	−1.91	1.83	90
$(Me_5Cp)_2VI_2$	54	2.024	2.000	1.990	2.000	56	88	18	0.95	0.04	60	81	−1.79	1.73	75
$(Me_5Cp)_2VIBr$	56	2.016	1.998	1.989	2.000	58	91	18	0.96	0.04	62	83	−1.85	1.77	85
$(Me_5Cp)_2VICl$	58	2.011	1.995	1.986	2.000	62	90	19	0.97	0.03	62	81	−1.85	1.73	75
$(Me_5Cp)_2V(NCS)_2$	63	1.994	1.992	1.987	2.000	65	104	19	0.95	0.05	68	94	−2.03	2.01	105

^{a} $Cp^* = \eta\text{-}CH_3C_5H_4$; $\eta\text{-}(CH_3)_4C_5H$; $\eta\text{-}(CH_3)_5C_5$.
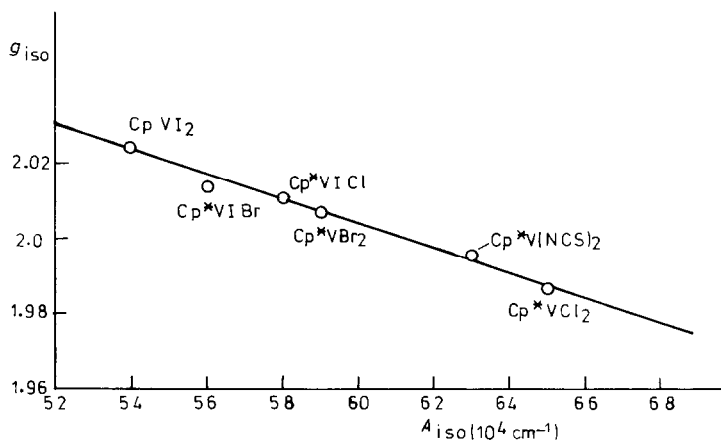
Fig. 1. Plot of g_{iso} against A_{iso} for $Cp_2^*V(X)(Y)$, $Cp^* = \eta$-C_5Me_5.

The g_{iso} and A_{iso} values for the mixed complexes Cp_2^*VXY (X = I, Y = Br, Cl), are intermediate between for the corresponding $Cp_2^*VI_2$ and $Cp_2^*VBr_2$ or $Cp_2^*VCl_2$ derivatives. However, these mixed complexes slowly decompose in solution at room temperature, as a result of rearrangement reactions, as can be seen from the EPR spectra.

The quantity $\Delta g = \langle g_{iso} \rangle - 2.0023$, is related to the energetic separation between the fundamental and the excited states, in agreement with the following expression [15].

$$\Delta g = 1/3 \sum |\lambda_M(A_1) + \lambda_{lig}(Bi)| / \Delta Ei$$

where λ_M and λ_{lig} are the spin-orbit coupling constants for the metal and ligands respectively, A_1 is the wave function of the fundamental state of C_{2v} symmetry in this case and Bi that for the excited state. The ΔEi values for the observed electronic transitions of the complexes are shown in Table 4 and although the assignments are not very certain it is evident that there is no large variation in ΔEi as the halogen ligands are varied.

TABLE 4

BAND MAXIMA (cm^{-1}, CHCl$_3$ solution) IN THE VISIBLE-UV ABSORPTION SPECTRA OF $(\eta$-$Cp^*)_2VXY$

Complexes	$d \leftarrow d$ transition	Charge transfer Metal $\leftarrow$ ring
$(MeCp)_2VCl_2$	13544	23100
$(MeCp)_2VBr_2$	13600	23800
$(MeCp)_2VI_2$	13800	26000
$(MeCp)_2V(NCS)_2$	14300	22700
$(Me_5Cp)_2VCl_2$	13500	22700
$(Me_5Cp)_2VBr_2$	13580	23000
$(Me_5Cp)_2VI_2$	13800	25000
$(Me_5Cp)_2V(NCS)_2$	14200	22200
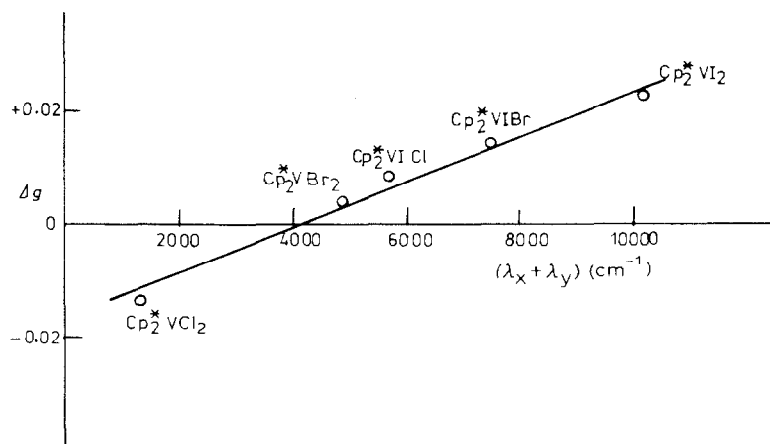
Fig. 2. Plot of Δg against $(\lambda_X + \lambda_Y)$ for $Cp_2^*V(X)(Y)$, $(Cp^* = \eta\text{-}C_5Me_5)$.

The band corresponding to the ring-metal charge transfer is shifted to lower frequencies as the number of methyl groups in the ring is increased, which reflects the higher electronic donation and oxidability of the Me_5Cp^- ligands. Similar behaviour has been found for other titanium cyclopentadienyl complexes [16]. As expected there is a linear relation between Δg and the amount $(\lambda_X + \lambda_Y)$ (see Fig. 2).

The anisotropic spectra of frozen solutions in mixtures of $CHCl_3$ and EtOH at liquid N_2 temperature show two well resolved sets of hyperfine lines (Fig. 3) and a

Fig. 3. EPR spectrum of $(\eta\text{-}C_5Me_5)_2V(NCS)_2$ in $CHCl_3$/EtOH glass at $-160°C$.

third poorly resolved set for which the g value and the hyperfine coupling constant can be calculated by use of the equations $g_{iso} = 1/3(g_x + g_y + g_z)$ and $A_{iso} = 1/3(A_x + A_y + A_z)$. The values for g and A so derived are listed in Table 3.

On basis of the ligand field model used by Petersen and Dahl to explain the EPR spectrum of $(\eta\text{-MeCp})_2\text{VCl}_2$ [17], the character of the metal orbital of the unpaired electron can be inferred from the hyperfine coupling parameters. In this model the fundamental state has A_1 symmetry, in which the relative contribution of the metal orbitals takes the form $|\psi_0\rangle = a|d_{z^2}\rangle + b|d_{x^2-y^2}\rangle$, where a and b are the mixing coefficients. By use of equations derived by Evans [18], the a and b values can be calculated, along with the corresponding EPR parameters, χ, P, K, $\langle r^{-3}\rangle$ and λ. The results are shown in Table 3.

The a^2 and b^2 values indicate that the unpaired electron is essentially located in a d_{z^2} orbital, in agreement with Petersen and Dahl's model. The P and $\langle r^{-3}\rangle$ values are related to the positive charge on the metal and the degree of covalent character in the bonds of the complex. The decrease in the values of P and $\langle r^{-3}\rangle$ indicate an increase in the covalent character of the complex. Values of 10^4P lie in the range 80–106 cm^{-1}, which, when compared with the P value for V^{4+} of 172×10^{-4} cm^{-1}, indicates that the unpaired electron is approximately 46–61% localized on the metal. The values of P and $\langle r^{-3}\rangle$ decrease on going from Cp$_2^*$VCl$_2$ to Cp$_2^*$VI$_2$, as expected.

The values of the spin polarization parameter K are not very different from those of A_{iso}, because $A_{iso} = -K + (g_{iso} - g_e)P$, and also fall when the degree of covalent character falls.

The contact term, χ, has slightly more positive values than those found by McGarvey [19] for a wide variety of vanadium(IV) complexes, which indicates that there is a small contribution of the $4s$ orbital to the fundamental state.

The observed variation in the negative values of χ (Table 3) indicates an increase in the $4s$ character of the unpaired electron as the covalence of the complex increases.

Experimental

All reactions were carried out under oxygen-free N$_2$. Tetramethylcyclopentadiene [20], pentamethylcyclopentadiene [21], $(\eta\text{-MeCp})_2\text{V}$ [22], $(\eta\text{-Me}_4\text{Cp})_2\text{V}$ [23] and $(\eta\text{-Me}_5\text{Cp})_2\text{V}$ [13] were prepared by published methods. The IR spectra were recorded at 4000–200 cm^{-1} on a Nicolet 5DX FT-IR spectrophotometer using Nujol and Hostaflon mulls between CsI windows. The spectra in the range 300–80 cm^{-1} were also recorded on a Nicolet 170 SX FT-IR using Nujol mulls between polyethylene windows.

The EPR spectra were recorded on a Varian E-12 spectrometer at a microwave frequency of 9 GHz (X-band) equipped with a HP 5342 A frequency meter, and a Bruker NMR Gauss meter. The visible-UV spectra are recorded on a Pye-Unicam SP8-100 spectrophotometer.

Preparation of compounds

$(\eta\text{-Me}_5\text{Cp})_2\text{VCl}_2$. A solution of PCl$_3$ (0.82 g, 6 mmol) was slowly added dropwise to a solution of freshly sublimed $(\eta\text{-Me}_5\text{Cp})_2\text{V}$ (1 g, 2.9 mmol) in anhydrous Et$_2$O (50 cm^3) saturated with oxygen free N$_2$. A green solid immediately

appeared, and this was filtered off, washed several times with Et_2O, and dried in vacuo. The yield was quantitative.

(η-Me₅Cp)₂V(NCS)₂. A solution of 1.5 g (12.9 mmol) of $(SCN)_2$ in 30 ml of diethyl ether, cooled to $-20°C$, is slowly added dropwise to a solution of (η-Me₅Cp)₂V in 50 ml of anhydrous and oxygen-free diethyl ether at $-20°C$. A green solid immediately appeared, and was filtered off on a cooled sintered glass disk $(-20°C)$, washed several times with cold diethyl ether, and dried in vacuum. The yield was quantitative.

Details of the preparation of the other complexes are given in Table 5.

TABLE 5

PREPARATIVE AND ANALYTICAL DATA FOR PRODUCTS

Complex	Cp*₂V [a] g (mmol)	PX₃,IX or (SCN)₂ g (mmol)	Analysis (Found (Calcd.)(%))						
			C	H	N	V	Cl	Br	I
(MeCp)₂VCl₂	1.0(4.8)	1.4(10.2)	51.0 (51.4)	4.8 (5.0)		18.0 (18.2)	24.9 (25.3)		
(MeCp)₂VBr₂	1.0(4.8)	2.7(10)	38.7 (3.9)	3.6 (3.7)		13.1 (13.8)		42.8 (43.3)	
(MeCp)₂VI₂	1.0(4.8)	4.10(10)	30.8 (31.1)	2.9 (3.0)		10.8 (11.0)			54.2 (54.8)
(MeCp)₂VICl	1.0(4.8)	0.8(5)	38.2 (38.7)	3.5 (3.7)		13.2 (13.7)	9.1 (9.5)		33.8 (34.1)
(MeCp)₂VIBr	1.0(4.8)	1(5)	33.9 (34.6)	3.2 (3.3)		11.8 (12.2)		18.9 (19.2)	29.7 (30.5)
(Me₄Cp)₂VCl₂	1.0(2.9)	0.8(6)	58.8 (59.3)	7.0 (7.1)		13.7 (14.0)	19.0 (19.5)		
(Me₄Cp)₂VBr₂	1.0(2.9)	1.6(6)	47.0 (47.6)	5.4 (5.7)		10.8 (11.2)		34.8 (35.3)	
(Me₄Cp)₂VI₂	1.0(2.9)	2.5(6)	39.0 (39.4)	4.6 (4.7)		8.9 (9.3)			45.8 (46.4)
(Me₄Cp)₂VICl	1.0(2.9)	0.5(3)	47.1 (47.4)	5.5 (5.7)		10.9 (11.2)	7.1 (7.8)		27.0 (27.8)
(Me₄Cp)₂VIBr	1.0(2.9)	0.6(3)	42.9 (43.2)	4.9 (5.2)		9.8 (10.2)		15.7 (16.0)	24.8 (25.0)
(Me₅Cp)₂VCl₂	1.0(3)	0.9(7)	59.8 (61.2)	7.4 (7.6)		12.8 (13.0)	17.9 (18.1)		
(Me₅Cp)₂VBr₂	1.0(3)	1.9(7)	49.1 (49.8)	6.0 (6.2)		10.0 (10.6)		32.9 (33.2)	
(Me₅Cp)₂VI₂	1.0(3)	2.8(7)	41.2 (41.7)	4.9 (5.2)		8.1 (8.8)			44.3 (44.1)
(Me₅Cp)₂VICl	1.0(3)	0.5(3.2)	49.3 (49.6)	6.0 (6.2)		10.1 (10.5)	6.9 (7.3)		25.8 (26.2)
(Me₅Cp)₂VIBr	1.0(3)	0.6(3.2)	45.0 (45.4)	5.3 (5.6)		9.1 (9.6)		14.9 (15.5)	23.7 (24.0)
(MeCp)₂V(NCS)₂	2.0(10.0)	1.5(12.9)	51.0 (51.7)	4.0 (4.3)	8.3 (8.6)	15.0 (15.7)			
(Me₄Cp)₂V(NCS)₂	2.9(10.0)	1.5(12.9)	58.1 (58.6)	6.0 (6.3)	6.2 (6.8)	11.9 (12.4)			
(Me₅Cp)₂V(NCS)₂	3.2(10.0)	1.5(12.9)	59.8 (60.4)	6.4 (6.8)	6.0 (6.2)	11.0 (11.6)			

[a] Cp* = MeCp, Me₄Cp, Me₅Cp.

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Acknowledgements

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