# ORGANOMETALLICS

# Formation of $[Cr(CO)_{x}(Ph_{2}PN(iPr)PPh_{2})]^{+}$ Structural Isomers by Reaction of Triethylaluminum with a Chromium N,N-Bis(diarylphosphino)amine Complex [Cr(CO)<sub>4</sub>(Ph<sub>2</sub>PN(*i*Pr)PPh<sub>2</sub>)]<sup>+</sup>: An **EPR and DFT Investigation**

Emma Carter,<sup>\*,†</sup> Kingsley J. Cavell,<sup>\*,†</sup> William F. Gabrielli,<sup>‡</sup> Martin J. Hanton,<sup>‡</sup> Andrew J. Hallett, Lucia McDyre,<sup>†</sup> James A. Platts,<sup>†</sup> David M. Smith,<sup>‡</sup> and Damien M. Murphy<sup>\*,†</sup>

<sup>†</sup>School of Chemistry, Cardiff University, Cardiff, CF10 3AT, U.K. <sup>‡</sup>Sasol Technology (U.K.) Ltd, Purdie Building, North Haugh, St Andrews, U.K.



ABSTRACT: The interaction of triethylaluminum (TEA) with a solution of the paramagnetic Cr(I) bis(phosphine) complex  $[Cr(CO)_4]$  [Al(OC(CF<sub>3</sub>)<sub>3</sub>)<sub>4</sub>] (1 = Ph<sub>2</sub>PN(*i*Pr)PPh<sub>2</sub>) has been studied using EPR and DFT. It was found that the TEA is responsible for the complete removal of all CO groups from the  $[Cr(CO)_41]^+$  complex, producing the  $[Cr(1-bis-\eta^6-arene)]^+$ , and this reaction occurs via a dominant pathway involving a series of  $[Cr(CO)_x 1]^+$  (x < 4) intermediates, consistently including the  $cis-[Cr(CO)_{3}1]^{+}$  complex (species A) and the "piano-stool"-type  $[Cr(CO)_{2}1]^{+}$  complex (species C). A further  $[Cr(CO)_{2}1]^{+}$ intermediate complex (labeled species D, which is a structural isomer of species C) was also identified experimentally, suggesting a second pathway for TEA activation may also be operative. All of these paramagnetic complexes have been characterized by CW EPR, and the spin Hamiltonian parameters were verified using DFT. The distribution and type of  $[Cr(CO), 1]^+$  intermediates formed were found to be very sensitive to the experimental conditions, including the quantity and manner of TEA addition, the temperature of activation, and the aging time of the solution.

# INTRODUCTION

The selective production of linear  $\alpha$ -olefins, particularly 1hexene and 1-octene, is a highly desirable reaction that has attracted significant academic and industrial interest over the past 20 years.<sup>1</sup> Among the many catalysts available for olefin oligomerization, chromium complexes have emerged as promising systems for both selective trimerization and tetramerization.<sup>1</sup> Ligands based on bis(phosphino)amine and bis(sulfanyl)amine<sup>2-4</sup> have been investigated in detail, but despite the enormous potential of these catalysts, the precise nature of the active species remains elusive.<sup>1</sup>

These catalysts are usually generated in situ by addition of a cocatalyst, such as an aluminum alkyl or an alkylaluminoxane.<sup>1</sup> The choice and indeed quantity (molar ratio of cocatalyst to chromium) of the cocatalyst significantly affects the outcome of the reaction,<sup>2d,e,5</sup> and it is reported to play various roles including an alkylating agent,<sup>6</sup> a reducing agent for chromium,<sup>2e,3,7</sup> aiding the formation of a cationic complex,<sup>2e,6b,8</sup> and scavenging impurities.<sup>8</sup> Furthermore, although several papers have appeared on the correlation between ligand structure and reaction selectivity,<sup>1,9</sup> the relationship is only

partly understood and empirically derived; a complete picture based upon the fundamental understanding is certainly more desirable, but as yet remains elusive. Nevertheless differences in both activity and selectivity of the catalytic reaction can still be tuned depending on which ligand is used.<sup>2a,4c</sup>

In parallel with the work reported on catalyst development and ligand design, the mechanistic aspects of the trimerization and tetramerization reaction have also been investigated in some detail both experimentally and theoretically.<sup>1</sup> Evidence has been presented that supports a Cr(II/IV) redox couple,<sup>1,10</sup> but Cr(I/III) centers have also been implicated in the catalysis,<sup>1b,11</sup> which operates via a metallacycle intermediate. While Cr(III) catalysts have certainly received considerable attention from the mechanistic perspective, fewer studies have explored the corresponding Cr(I) complexes.<sup>12</sup> We therefore recently examined the structure of a family of low-valent paramagnetic Cr(I) complexes of general formula [Cr- $(CO)_4L^{\dagger}$  (where L = Ph<sub>2</sub>PN(R)PPh<sub>2</sub>, Ph<sub>2</sub>P(R)PPh<sub>2</sub>) using



Received: January 14, 2013

electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) spectroscopy.<sup>13</sup> Despite the differences in the structure of the diphosphine ligand in these complexes, no correlation was noted between the observed spin Hamiltonian parameters and the catalytic ethylene tetramerization data, indicating that the structure of the active catalyst was significantly different compared to the  $[Cr(CO)_4L]^+$  precatalysts.<sup>13</sup> We then monitored the structural changes to two specific  $[Cr(CO)_4L]^+$  complexes  $(L = Ph_2PN(iPr)PPh_2$  and  $Ph_2P(C_3H_6)PPh_2$  following the addition of 10 molar equiv of triethylaluminum (Et<sub>3</sub>Al, hereafter labeled TEA) at room temperature and identified the formation of a Cr(I) bis-arene complex, labeled  $[Cr(L-bis-\eta^6-arene)]^+$ .<sup>14</sup> This complex was shown to arise from an intramolecular rearrangement and coordination of Cr(I) to the ligand phenyl groups and indicated that the TEA was responsible for complete loss of the CO ligands (Scheme 1).<sup>14</sup>

Scheme 1. Structure of the  $[Cr(CO)_4Ph_2PN(iPr)PPh_2]^+$ Complex Investigated Here (Labeled  $[Cr(CO)_41]^+$ ) and Associated Counterion<sup>*a*</sup>



<sup>*a*</sup>The transformation of  $[Cr(CO)_4\mathbf{1}]^+$  into a bis-arene species  $[Cr(\mathbf{1}-bis-\eta^6-arene)]^+$  by TEA addition is also shown.

Following on from these initial experiments we sought to explore further the possibility that other partially decarbonylated  $[Cr(CO)_x L]^+$  (x < 4) intermediates may also be involved in the above transformations and can therefore be identified by EPR and DFT following activation of the  $[Cr(CO)_4L]^+$ complexes using varying levels of TEA at specific temperatures. Herein, we describe the structure of the paramagnetic Cr(I)intermediates formed after activating a solution of the  $[Cr(CO)_4(Ph_2PN(iPr)PPh_2)]^+$  complex  $([Cr(CO)_41]^+;$  see Scheme 1) using varying ratios of TEA (from 0.5 to 10 equiv) at different temperatures. EPR spectroscopy, in conjunction with DFT, reveals how different intermediate  $[Cr(CO)_{3}1]^{+}$  and  $[Cr(CO)_{2}1]^{+}$  complexes can be formed in the solution. This work highlights the structural variety of Cr(I)complexes that may exist in these oligomerization catalysts  $[Cr(CO)_4L]^+$ , even when very low levels of cocatalyst (TEA) are present.

#### RESULTS AND DISCUSSION

**EPR Spectroscopy.** The low-temperature continuous wave (CW) EPR spectrum of the  $[Cr(CO)_41]^+$  complex in frozen solution is shown in Figure 1a. The main features of this



**Figure 1.** X-band CW EPR spectra of (a)  $[Cr(CO)_41]^+$  (1 = Ph<sub>2</sub>PN(*i*Pr)PPh<sub>2</sub>) dissolved in dichloromethane (recorded at 140 K) and (b)  $[Cr(1-bis-\eta^6-arene)]^+$  formed after addition of 10 molar equiv of TEA to  $[Cr(CO)_41]^+$  (recorded at 185 K). An expanded view of the  $[Cr(1-bis-\eta^6-arene)]^+$  signal is shown in the inset. The corresponding simulations are shown in a' and b'.

spectrum were recently discussed in detail by us, as part of a study on a series of related  $[Cr(CO)_4L]^+$  complexes  $(L = Ph_2PN(R)PPh_2, Ph_2P(R)PPh_2)$ .<sup>13</sup> In brief, this EPR spectrum is characterized by an axial g tensor  $(g_{\perp} > g_e > g_{\parallel})$  with a large hyperfine coupling originating from two equivalent <sup>31</sup>P nuclei (Table 1). The spin Hamiltonian parameters were shown to be consistent with a low-spin d<sup>5</sup> Cr(I) center possessing a SOMO of largely  $d_{xy}$  character.<sup>13,15</sup>

Following the 298 K addition of 10 molar equiv of TEA:Cr into a dichloromethane solution of  $[Cr(CO)_4 1]^+$ , the EPR spectrum changes completely and a narrow symmetrical signal with well-resolved <sup>1</sup>H hyperfine couplings can now be observed at 185 K (Figure 1b). For clarity only the fluid solution spectrum is shown in Figure 1b, to highlight the distinctive <sup>1</sup>H couplings, since the corresponding low-temperature spectrum (recorded at 140 K) does not display any resolved hyperfine structure.<sup>14</sup> An analogous spectrum to that shown in Figure 1b was recently reported by us<sup>14</sup> and shown to arise from a Cr(I) bis-arene complex, labeled  $[Cr(2-bis-\eta^6-arene)]^+$  (where 2 =Ph<sub>2</sub>P(C<sub>3</sub>H<sub>6</sub>)PPh<sub>2</sub>), but identical EPR spectra are observed with ligand 1.<sup>14</sup> Figure 1b was obtained in dichloromethane, since solvent-based  $[Cr(bis-arene)]^+$  complexes are preferentially formed in the presence of aromatic solvents, such as toluene, upon addition of TEA.<sup>14</sup>

The well-resolved multiplet pattern in Figure 1b originates from the hyperfine interaction with 10 equivalent <sup>1</sup>H's of the  $\eta^{6}$ -coordinated phenyl rings in 1, as expected in this particular Cr(I) bis-arene species (Scheme 1).<sup>14</sup> Under the adopted experimental conditions (i.e., addition of 10 equiv of TEA at 298 K), ca. 80% of the original EPR signal is lost following activation of [Cr(CO)<sub>4</sub>1]<sup>+</sup>, as the signal intensity decreases substantially from Figure 1a to 1b.<sup>16</sup> The entire remaining spectral intensity in Figure 1b arises from the [Cr(1-bis- $\eta^{6}$ arene)]<sup>+</sup> species. No other paramagnetic Cr(I) or Cr(III) centers were detected under these specific activation con-

Table 1. Spin Hamiltonian Parameters for the Series of Cr(I) Diphenylphosphino-Based Complexes  $[Cr(CO)_41]^+$ ,  $[Cr(CO)_21]^+$ , and  $[Cr(1-bis-\eta^6-arene)]^{+\alpha}$ 

		g values				<sup>P</sup> A values <sup>b</sup>				
species		<i>g</i> <sub>1</sub>	<i>g</i> <sub>2</sub>	<i>g</i> <sub>3</sub>	$g_{\rm iso}$	$A_1$	$A_2$	A <sub>3</sub>	a <sub>iso</sub>	refs
$[Cr(CO)_41]^+$	expt	2.072	2.072	1.988	2.044	$\pm 78.30$	$\pm 78.30$	±71.00	±75.90	13, this work
	DFT	2.0470	2.0369	1.9944	2.0261	-99.753	-82.695	-82.149	-88.199	
$[Cr(CO)_4 2]^{+f}$	expt	2.063	2.063	1.987	2.037	±72.0	±72.0	<u>±68.1</u>	±70.7	13
	DFT	2.0436	2.0339	1.9910	2.0228	-80.400	-71.528	-69.329	-73.752	
(species A) cis-[Cr(CO) <sub>3</sub> 1] <sup>+</sup>	expt	2.032	2.017	1.988	2.012	$\pm 55.44^{c}$	$\pm 40.60^{c}$	$\pm 41.86^{c}$	±45.96	this work
	DFT	2.0541	2.0299	1.9967	2.0269	-82.04	-70.49	-69.73	-74.09	
						-87.39	-76.21	-75.02	-79.54	
(species B) trans- $[Cr(CO)_31]^+$	DFT	2.0328	2.0176	1.962	2.0043	-119.09	-95.83	-94.88	-103.3	this work
						-81.0	-71.55	-69.4	-74.28	
(species C) $[Cr(CO)_2 1]^+$	expt	2.043	2.010	1.994	2.015	$\pm 54.88^{d}$	$\pm 66.40^{d}$	$\pm 56.28^{d}$	±59.18	this work
	DFT	2.0537	2.0225	1.9948	2.0237	-112.896	-95.380	-91.538	-99.938	
						-7.809	-6.855	-4.342	-6.335	
(species D) $[Cr(CO)_2 1]^+$	expt	2.014	2.014	1.970	1.999	<u>+</u> 86.80	<u>+</u> 86.80	±98.0	±90.50	this work
	DFT	2.0247	2.0120	1.9209	1.9859	-106.39	-107.925	-129.908	-114.66	
$[Cr(1-bis-\eta^6-arene)]^+$	expt <sup>e</sup>	1.979	1.979	2.003	1.987					14
	$\mathrm{DFT}^{e}$	1.9771	1.9771	2.0027	1.9856					
[Cr(3)] <sup>+</sup>		2.007	1.995	1.979	1.993					20a
[Cr(4)] <sup>+</sup>		2.010	1.997	1.975	1.994					20b
$[Cr(5)]^+$		2.104	2.013	1.994	2.037	±95.20	±100.80	<u>+</u> 98.00	±98.00	20c, d
[Cr(6)] <sup>+</sup>		2.134	2.035	1.997	2.055					20e, f

<sup>*a*</sup>For comparison the *g* values for a range of piano-stool-type complexes (labeled  $[Cr(3-6)]^+$ ; Scheme 2) are also given. Errors:  $g = \pm 0.005$ ;  $A_i = \pm 0.50$  MHz. <sup>*b*</sup>All hyperfine values are given in MHz. <sup>*c*</sup>Coupling arises from two equivalent <sup>31</sup>P nuclei. <sup>*d*</sup>The smaller <sup>31</sup>P coupling was not detected in the experimental spectrum. <sup>*c*</sup>Only the *g* values are given (see ref 14 for the <sup>1</sup>H and <sup>53</sup>Cr couplings). <sup>*f*</sup>For comparison purposes, the experimental (taken from ref 13) and calculated (DFT)  $g/^{P}A$  values for a second Cr(I) complex,  $[Cr(CO)_42]^+$  ( $2 = Ph_2P(C_3H_6)PPh_2$ ), are also reported.

ditions, to account for the ca. 80% loss in signal intensity.<sup>14</sup> However, when the  $[Cr(CO)_41]^+$  complex is exposed to lower levels of TEA (less than 10 equiv) and crucially when the activation temperature is lowered to 273 K (rather than 298 K), a different series of EPR signals can be detected (as shown in Figures 2 and 3).

First when 2 equiv of TEA is added directly to a dichloromethane solution of  $[Cr(CO)_41]^+$  at 273 K and the sample is immediately cooled to 140 K, a new EPR spectrum can be observed (Figure 2a). This spectrum contains overlapping features bearing a significant contribution from residual, unreacted  $[Cr(CO)_41]^+$  (labeled *Precatalyst* in Figure 2a). However, additional signals are also clearly visible in this spectrum (compare Figure 1a to 2a). As the sample is progressively and slowly warmed from 140 K to 298 K, the EPR spectra evolve as the distribution of these new signals changes (from Figure 2a to 2b,c). Eventually after aging the sample overnight at 298 K, only the anisotropic frozen solution EPR signal of the bis-arene  $[Cr(1-bis-\eta^6-arene)]^+$  complex remains (Figure 2d, recorded at 140 K). It should be recalled that an analogous EPR spectrum to Figure 2d can also be formed simply by addition of 10 molar equiv of TEA directly at 298 K (as in Figure 1b).

The new signals detected in Figure 2a–c most likely arise from "intermediate" partially decarbonylated complexes, of the form  $[Cr(CO)_x 1]^+$  (x < 4), since their profile is quite distinctive and different from the EPR spectra observed for the two limiting cases of  $[Cr(CO)_4 1]^+$  and  $[Cr(1-bis-\eta^6-arene)]^+$  (Figure 1). The relative abundance of these "intermediate" complexes, as monitored by EPR, was also found to vary slightly from one experiment to the next and crucially was very dependent on how the TEA was added (suggesting they are not particularly stable species or the interaction of TEA with the Cr(I) complex is difficult to control). For example, direct addition of 10 equiv of TEA at 298 K leads to the observation of the  $[Cr(1-bis-\eta^6-arene)]^+$ complex only (vide supra, Figure 1), but if small aliquots of TEA ( $\approx 1$  equiv) are slowly and progressively added to the solution at 273 K, then these intermediate complexes can still be detected even when the total cumulative TEA quantity reaches 10 equiv; eventually after overnight aging at 298 K, the  $[Cr(1-bis-\eta^6-arene)]^+$  species can be detected. These results may initially be simply the result of the slower rate of formation of  $[Cr(1-bis-\eta^6-arene)]^+$  at 273 K versus 298 K. In other words, direct addition of 10 equiv of TEA at 298 K gives the bis-arene signal immediately (with no other signals), and the stepwise addition of 10 equiv of TEA in small aliquots at 298 K produces a bis-arene signal within ca. 1 h, whereas small quantities of TEA added at 273 K produce only the bis-arene after prolonged aging (overnight). Generally, these intermediate complexes shown in Figure 2 could not be detected under any conditions if the TEA levels were higher than 5 equiv.

Furthermore, in an experiment performed with the direct addition of 5 equiv of TEA at 293 K, a new additional intermediate species was detected (Figure 3). The well-resolved axial  $g/{}^{P}A$  profile for this spectrum is quite distinct from the spectra of the intermediate species shown in Figure 2a-c, suggesting that this new spectrum in Figure 3 (with very intense Cr(I) signals, comparable to the precatalyst [Cr-(CO)<sub>4</sub>1]<sup>+</sup> signal intensities) must arise from a further intermediate complex. The absence of any bis-arene signal in this spectrum (Figure 3) may also imply that a different activation pathway has been followed in this case (*vide infra*).

Therefore, in order to identify the nature of these newly formed paramagnetic centers responsible for the EPR spectra shown in Figures 2 and 3, we performed a series of DFT



**Figure 2.** X-band CW EPR spectra of (a)  $[Cr(CO)_41]^+$  dissolved in dichloromethane following the addition of 2 molar equiv of TEA at 273 K and immediately frozen to 140 K. The sample was then warmed to (b) 200 K and (c) 273 K for 30 min and (d) left at 298 K overnight. All spectra were recorded at 140 K. The simulations (shown in a', b', c', and d') were obtained using different contributions of  $[Cr-(CO)_41]^+$ , species A  $([Cr(CO)_31]^+)$ , species C  $([Cr(CO)_21]^+)$ , and  $[Cr(1-bis-\eta^6-arene)]^+$ . The relative weightings of these four species in the simulations were respectively (a') 0.55:0.33:0.0:0.12, (b') 0.0:0.66:0.19:0.15, (c') 0.0:0.35:0.35; and (d') 0.0:0.0:0.0:1.0. See Scheme 3 for structures of species A and C.

calculations to ascertain the magnitude of the spin Hamiltonian parameters for a series of plausible  $[Cr(CO)_x 1]^+$  intermediate complexes.

DFT Calculations. The experimentally determined spin Hamiltonian parameters (g and  ${}^{P}A$ ) for  $[Cr(CO)_{4}L]^{+}$  (L =  $Ph_2PN(R)PPh_2$ ,  $Ph_2P(R)PPh_2$ ) and  $[Cr(1-bis-\eta^6-arene)]^+$  have been reported recently by us.<sup>13,14</sup> We therefore decided to first calculate these parameters as a reference point using DFT, before examining the possible  $[Cr(CO)_r 1]^+$  intermediates formed by addition of TEA. The calculated g and  ${}^{P}A$  values for  $[Cr(CO)_41]^+$  are listed in Table 1 along with the experimental values. The spin Hamiltonian parameters for the  $[Cr(CO)_4L]^+$  complexes were experimentally found to vary depending on the nature of L,<sup>13</sup> specifically with variations in the  $g_{iso}$  and  ${}^{P}a_{iso}$  values (Table 1).<sup>13</sup> Although current state-ofthe-art DFT cannot quantitatively predict the EPR parameters of transition metal ions,<sup>17</sup> the general agreement between the experimental and calculated values for the precatalyst [Cr- $(CO)_4 1$ <sup>+</sup> is very good. It is important to note that DFT overestimates the <sup>P</sup>A values in  $[Cr(CO)_4 1]^+$  compared to the experiments. Furthermore, the experimental and calculated parameters for the bis-arene  $[Cr(1-bis-\eta^6-arene)]^+$  complex<sup>14</sup> were also found to be satisfactorily reproduced by DFT (Table 1).



**Figure 3.** X-band CW EPR spectra of  $[Cr(CO)_41]^+$  dissolved in dichloromethane following the addition of 5 molar equiv of TEA. These spectra have been assigned to species D ( $[Cr(CO)_21]^+$ ). The spectra were recorded at (a) 140 K and (b) 298 K. The corresponding simulations are shown in a' and b'. Note:  $[Cr(CO)_41]^+$  produces a broad, structureless signal at 298 K due to fast relaxation characteristics, whereas a readily resolved EPR signal can still be detected at the same temperature for species D. See Scheme 3 for structure of species D.

With good agreement achieved between experiment and theory on this parent complex, we next calculated the spin Hamiltonian parameters for the two structural isomers of  $[Cr(CO)_31]^+$  (i.e., starting from the octahedral geometry of  $[Cr(CO)_41]^+$ , one CO was removed from a position either *cis* or *trans* to the P atom, and the resulting structure allowed to relax to the geometry-optimized complex shown in Figure 4); hereafter these two isomers are labeled species A and B (see Figure 4). In addition we also calculated the spin Hamiltonian



**Figure 4.** DFT-optimized structures of the precatalyst  $[Cr(CO)_41]^+$  and the proposed intermediate  $[Cr(CO)_31]^+$  (species A and B) and  $[Cr(CO)_21]^+$  (species C and D) complexes.

parameters for the two structural isomers of  $[Cr(CO)_21]^+$ , hereafter labeled species C and D (Figure 4). The energy differences within each set of isomers were found to be substantial. The *cis*- and *trans*- $[Cr(CO)_31]^+$  complexes differed in energy by only 20 kJ mol<sup>-1</sup>, with the *cis*-complex (species A) being more stable; both isomers are 15-electron complexes. For the  $[Cr(CO)_21]^+$  isomers, the differences were even more substantial, with the 17-electron piano-stool isomer (species C) being 120 kJ mol<sup>-1</sup> more stable compared to the 13-electron species D. The DFT-calculated g and <sup>P</sup>A values, along with the known g values for related Cr(I) complexes, were then used as a starting point to assist in the interpretation and deconvolution of the EPR spectra shown in Figures 2 and 3.

Nature of the Intermediate Complexes and Analysis of the Spin Hamiltonian Parameters. A detailed review of the EPR parameters for a wide range of low-spin d<sup>5</sup> transition metals, including Cr(I)-carbonyl complexes, has previously been presented by Rieger.<sup>15</sup> In most cases, axial or slightly rhombic *g* tensors are reported for the pseudo-octahedral complexes with a predominantly  $d_{xy}$  ground state.<sup>18</sup> This is indeed the situation observed for the  $[Cr(CO)_41]^+$  complex possessing well-defined axial *g* and <sup>P</sup>A values (Table 1). On the other hand, the d<sup>5</sup> sandwich complexes of Cr(I) produce easily recognizable EPR signals because the SOMO is largely  $d_{z^2}$  in character.<sup>15,19</sup> Since the  $e_{1g}$  orbital containing most of the  $d_{xy}$  $d_{yz}$  character lies well above the SOMO, negative *g* shifts are expected in the EPR spectrum (i.e.,  $g_{\perp} < g_e$ ), as indeed observed for  $[Cr(1-bis-\eta^6-arene)]^+$  (Table 1).

By comparison, some of the low-symmetry  $[Cr(CO)_r 1]^+$ complexes, particularly the piano-stool species C, are expected to produce very distinctive EPR profiles with a rhombic gtensor<sup>15,20</sup> and should be easily identified. For example, representative g values for a series of Cr(I) piano-stool-type complexes (shown in Scheme 2) are listed in Table 1. Indeed, Cr(I) piano-stool-type complexes bearing a diphenylphosphino ligand (Scheme 2) have been structurally characterized in the past,<sup>21</sup> so their formation in the current system would not be unexpected. For  $[Cr(CO)_2 1]^+$  (species C), hyperfine couplings to two inequivalent <sup>31</sup>P nuclei and a rhombic g tensor are therefore expected,<sup>15</sup> and this prediction was nicely reproduced by DFT (Table 1), giving  $g_{iso} > g_e$  and inequivalent <sup>31</sup>P couplings ( ${}^{P1}a_{iso} = -99.93$  MHz and  ${}^{P2}a_{iso} = -6.335$  MHz). The <sup>1</sup>H couplings could not be experimentally detected, so we did not consider these. Using the DFT parameters calculated for species C and the literature values for Cr(I) piano-stool complexes,<sup>15</sup> the overlapping EPR spectra shown in Figure 2ac could then be simulated; the resulting spin Hamiltonian parameters used in the simulation are listed in Table 1 and were found to be in reasonable agreement with the theory (although the experimental <sup>P</sup>A values are significantly smaller).

Furthermore, a second intermediate complex was also found to contribute to the mixed EPR spectra in Figure 2a-c, as manifested by the evolving profile of the peaks as a function of increasing temperature. We considered that species A or B must also contribute to this mixed spectrum (since the predicted  $\Delta g$  values for species D are far too small; Table 1). Since species A was calculated to be more stable compared to species B (by 20 kJ mol<sup>-1</sup>), the DFT spin Hamiltonian parameters for A were used as a starting point in the simulation of Figure 2, specifically using a rhombic g tensor and large  $\Delta g$ shifts. The nearly equivalent <sup>31</sup>P nuclei in species A are largely responsible for the quasi 1:2:1 triplet pattern, which is just evident in Figure 2a,b. This signal decreases in intensity over Scheme 2. Representative Series of EPR-Characterized Cr(I)Piano-Stool-Type Complexes  $(3-6)^a$ 



<sup>*a*</sup>Two further examples of structurally characterized Cr(I) dicarbonyl piano-stool-type complexes bearing the diphenylphosphino ligand are the [bis(diphenylphosphino- $\eta$ -benzene)chromium]carbonyl complex (7) and the dicarbonyl bis(di-o-tolyl)phosphinomethane Cr(I) complex (8). See Table 1 for corresponding spin Hamiltonian parameters and references.

time with the concurrent increase of species C in Figure 2c (possessing rhombic g values, but with each g component split into a doublet due to the large <sup>P</sup>A coupling to the unique <sup>31</sup>P nucleus in the piano-stool complex). The series of spectra in Figure 2 could therefore be satisfactorily simulated using contributions from unreacted  $[Cr(CO)_41]^+$ ,  $[Cr(CO)_31]^+$  (species A),  $[Cr(CO)_21]^+$  (species C), and  $[Cr(1-bis-\eta^6-arene)]^+$ ; excellent agreement with the experimental spectra was obtained simply by varying the contribution (weighting) of these four paramagnetic complexes in each spectrum.

We were unable to reproduce the EPR spectra in Figure 2 by including any contributions from species B (i.e., characterized by a rhombic g tensor, but with inequivalent <sup>31</sup>P couplings). Therefore we may conclude that under these specific experimental conditions of TEA addition, only the intermediate species A and C were formed in the reaction pathway as the stable precatalyst  $[Cr(CO)_41]^+$  complex is progressively transformed into the relatively stable bis-arene  $[Cr(1-bis.\eta^{6}-arene)]^+$  complex via A and C (Scheme 3). It should also be recalled that according to DFT, the *cis*- $[Cr(CO)_31]^+$  structure (species B), so the absence of the latter intermediate from Figure 2 is not surprising.

Although the piano-stool complex (species C) was identified in Figure 2, the second structural isomer of  $[Cr(CO)_2 1]^+$ (species D) was not observed under these experimental conditions. According to the DFT calculations, this species is expected to possess the largest <sup>31</sup>P couplings ( $a_{iso} = -115.66$ MHz), smallest  $\Delta g$  shifts, and  $g_{iso}$  (=1.9859) <  $g_e$ , compared to the other intermediates. These parameters generally match the principal characteristics of the EPR spectrum shown in Figure 3a, which was recorded following addition of 5 molar equiv of TEA at 293 K. In particular small  $\Delta g$  shifts,  $g_{iso}$  (=1.999) <  $g_{ey}$  Scheme 3. Summary of the Transformations That Occur Following Activation of the Precatalyst  $[Cr(CO)_41]^+$  with Cocatalyst (TEA) in Dichloromethane Solvent<sup>*a*</sup>



<sup>a</sup>Other than species B, all of the above complexes were detected and characterized by EPR.

and large <sup>31</sup>P couplings were found experimentally ( $a_{iso} = \pm$  90.53 MHz). These parameters are quite distinct from the aforementioned lower symmetry species A, B, and C. The resulting spin Hamiltonian parameters extracted by simulation of the EPR spectra (Figure 3) are given in Table 1. Therefore based on the agreement between the DFT and EPR data, the spectrum shown in Figure 3 can be confidently assigned to species D. Since species D was calculated to be far less stable compared to species C (by 120 kJ mol<sup>-1</sup>), the observation of D in Figure 3 suggests that a different (or secondary) pathway may also occur during TEA activation of [Cr(CO)<sub>4</sub>1]<sup>+</sup>.

Transformations of [Cr(CO)<sub>4</sub>1]<sup>+</sup> Following TEA Addition. As mentioned earlier, the role played by TEA as a cocatalyst for reactions in olefin oligomerization varies enormously from an alkylating agent,<sup>6</sup> to a reducing agent for chromium,<sup>2e,3,7</sup> to aiding the formation of cationic complexes<sup>2e,6b,8</sup> to scavenging impurities.<sup>8</sup> According to the current EPR results, the addition of TEA is also responsible for the loss of paramagnetic Cr(I) signal intensity (Figures 1 and 2). Some of this loss is likely attributed to the formation of diamagnetic complexes, whose identity is currently unclear. However the residual EPR signals detected after TEA addition can certainly be assigned to various intermediate  $[Cr(CO)_x 1]^+$  complexes and eventually the stable  $[Cr(1-bis-\eta^6-arene)]^+$  complex. Addition of TEA therefore clearly leads to the elimination of some or all of the CO groups from the starting  $[Cr(CO)_41]^+$ complex. Preliminary 2P ESEEM experiments did not reveal any strong <sup>27</sup>Al modulation, so although TEA is responsible for elimination of CO, it does not coordinate to the Cr(I) centers (at least under the adopted experimental conditions). Although the experimental EPR spectra can be quite complex due to the simultaneous presence of multiple Cr(I) centers (Figure 2), the spin Hamiltonian parameters of the different "intermediate" species are sufficiently distinct that they can be readily identified in the experimental spectra.

It should be recalled that the Philips trimerization system is composed of a chromium source, 2,5-dimethylpyrrole, and  $Et_3Al^1$  and that it is believed to operate via a  $Cr^{II/IV}$  cycle, although Cr<sup>I/III</sup> have also been proposed.<sup>7c,11</sup> The pyrrole ligand is thought to flip between  $\eta^1$  and  $\eta^5$  coordination throughout the catalytic cycle, effectively compensating for changes in the coordination environment at the chromium center.<sup>1b</sup> Intriguingly the presence of the two structural isomers of [Cr- $(CO)_2 \mathbf{1}]^+$  (species C and D), one of which is  $\eta^6$  coordinated to a Ph ring of PPh<sub>2</sub>, could also imply that an intramolecular rearrangement of Cr(I) may also be possible in these diphenylphosphino ligand based catalysts. Certainly the facile formation of the bis-arene  $[Cr(1-bis-\eta^6-arene)]^+$  complex indicates the importance of  $\eta^6$  coordination modes in these systems. Clearly the structures of the paramagnetic Cr(I)complexes presented in Scheme 3 may not exist under the highpressure conditions operative during catalysis nor in the presence of ethylene or at higher cocatalyst levels. Nevertheless, the current findings reveal how the molecular rearrangement of the parent  $[Cr(CO)_41]^+$  complex can be transformed in solution simply by addition of low levels of cocatalyst (TEA), as  $[Cr(CO)_41]^+$  evolves into  $[Cr(1-bis-\eta^6-arene)]^+$  through the possible intermediates  $[Cr(CO)_31]^+$  (species A) and [Cr- $(CO)_2 \mathbf{1}^+$  (species C).

Finally it should be mentioned that the relative distribution of the intermediate species was observed to vary depending on how the TEA is added to a solution of the complex (in small aliquots or as a larger aliquot), how much is added (concentration), the temperature of addition (273 K versus 298 K), and the aging time. The relative distribution of the paramagnetic species, as extracted by simulations of the EPR spectra (see Figure 2 caption), therefore changes according to these experimental variables for TEA addition. In other words, a combination of  $[Cr(CO)_41]^+$ ,  $[Cr(CO)_31]^+$  (species A),  $[Cr(CO)_21]^+$  (species C), and  $[Cr(1-bis-\eta^6-arene)]^+$  was typically observed in the EPR spectra (as in Figure 2), but the relative weightings of each species varied slightly from one experiment to the next. Furthermore, the observation of the intermediate species D, obtained by using slightly different experimental conditions for TEA addition, only emphasizes the fact that controlling how the TEA is added, at what temperature, and for how long will affect the nature of the resulting species. These results therefore highlight the difficulty of structurally characterizing the nature of the complexes formed by addition of the cocatalyst, TEA, to a series of Cr(I) diphenylphosphino ligand based catalysts, as the nature and distribution of the paramagnetic Cr(I) "intermediate" complexes (species A, C, D, and finally  $[Cr(1-bis-\eta^6-arene)]^+)$  can vary greatly depending on the experimental conditions.

# CONCLUSION

A combined CW EPR spectroscopy and DFT computation study of a Cr(I)bis(phosphine) complex,  $[Cr(CO)_41]^+$ , has been carried out to investigate the progressive changes to the tetracarbonyl complex following the addition of small quantities of triethylaluminum. At ambient temperatures and pressures, addition of 10 molar equiv of TEA to a dichloromethane solution of  $[Cr(CO)_4 1]^+$  results in the formation of a bis-arene complex,  $[Cr(1-bis-\eta^6-arene)]^+$ , and complete loss of CO. Approximately 80% of the starting Cr(I) signal intensity (from  $[Cr(CO)_41]^+$  is lost at this stage. However, addition of 1–2 molar equiv of TEA at slightly lower temperatures (273 K) affords the detection of intermediate  $[Cr(CO), 1]^+$  complexes due to the partial loss of CO. The two structural isomers of  $[Cr(CO)_2 1]^+$ , namely, species C and D, were both detected by EPR (albeit under different TEA activation conditions). The more stable piano-stool-type complex, species C, was found to be more prevalent in the experiments. Among the two possible structural isomers of  $[Cr(CO)_3 1]^+$  (species A and B), only the former and slightly more stable species A was detected experimentally. The DFT-calculated spin Hamiltonian parameters were used as a starting point to simulate the overlapping EPR spectra, containing varying contributions of  $[Cr(CO)_41]^+$ ,  $[Cr(CO)_31]^+$  (species A),  $[Cr(CO)_21]^+$  (species C), and  $[Cr(1-bis-\eta^6-arene)]^+$ . As the temperature of the  $[Cr(CO)_41]^+/$ TEA (2 equiv) solution is raised, the loss of Cr(I) centers follows the following trend:  $[Cr(CO)_4\mathbf{1}]^+$  is depleted first, followed by  $[Cr(CO)_31]^+$  and  $[Cr(CO)_21]^+$ , until eventually only the  $[Cr(1-bis-\eta^6-arene)]^+$  signal is detected. The distribution and detection of the intermediate species are very sensitive to the quantity and manner of TEA addition. These results highlight the complexity of the paramagnetic species that can exist with Cr(I)bis(phosphine) complexes following interaction with a cocatalyst. While there is some variation in the ratios of intermediates generated during catalyst activation with TEA, depending on reaction conditions, it is clear that several key intermediates are consistently formed. This allows us to gain a better understanding of the activation process and the oxidation state(s) of the metal center that may be involved in the catalysis.

#### EXPERIMENTAL SECTION

All manipulations were performed using standard Schlenk techniques under an Ar or N<sub>2</sub> atmosphere in an MBraun UNILAB glovebox (less than 0.1 ppm H<sub>2</sub>O and O<sub>2</sub>). Solvents were dried using a Braun solvent purification system and degassed prior to use. Ligand **1** was prepared according to a literature procedure.<sup>22</sup> The chromium(0) and chromium(I) compounds of  $[Cr(CO)_41]^+$  were prepared according to literature procedures.<sup>12,23</sup> The  $Ag[Al(OC(CF_3)_3)_4]$  was prepared according to a literature procedure.<sup>24</sup>

**Instruments.** NMR spectra were recorded at 298 K on Bruker Avance AMX 400 or Jeol Eclipse 300 spectrometers. Chemical shift values are given relative to residual solvent peak. ESI-MS were performed on a Waters LCT Premier XE instrument. Infrared spectra were recorded using a JASCO FT/IR-660 Plus spectrometer and analyzed in solution (dichloromethane). Microanalyses were performed by SASOL Ltd. All continuous-wave EPR spectra were recorded on an X-band Bruker EMX spectrometer operating at 100 kHz field modulation, 10 mW microwave power, and equipped with a high-sensitivity cavity (ER 4119HS). EPR computer simulations were performed using the SimEPR32 program.<sup>25</sup> g values were determined using a DPPH standard.

Synthesis of Chromium(0) Tetracarbonyl Complex [Cr-(CO)<sub>4</sub>(Ph<sub>2</sub>PN(*i*Pr)PPh<sub>2</sub>)]. Toluene (20 mL) was added to chromium hexacarbonyl  $[Cr(CO)_6]$  (350 mg, 1.59 mmol) and 1 (500 mg, 1.17 mmol), and the stirred mixture was heated under reflux for 48 h. The solution was cooled to 0 °C and filtered to remove excess  $[Cr(CO)_6]$ . Solvent was removed under reduced pressure, and the product extracted into dichloromethane (5 mL). Methanol (10 mL) was added to precipitate the product, which was isolated by filtration and dried in *vacuo* to yield the yellow solid  $[Cr(CO)_4(Ph_2PN(iPr)PPh_2)]$ : yellow solid (260 mg, 38%); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.8 MHz, 298 K) δ (ppm) 0.62 (d, 6H, CH<sub>3</sub>,  $J_{HH}$  = 6.8 Hz), 3.52 (sept, 1H, CH,  $J_{HH}$  = 7.0 Hz), 7.41 (m, 12H, meta-, para- $C_6H_5$ ), 7.69 (m, 8H, ortho- $C_6H_5$ ); <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 121.7 MHz, 298 K) δ (ppm) 112.70 (s); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125.8 MHz, 298 K) δ (ppm) 22.54 (CH<sub>3</sub>), 54.79 (CH), 127.39 (meta- $C_6H_5$ ), 129.52 (para- $C_6H_5$ ), 130.86 (ortho- $C_6H_5$ ), 136.09 (ipso-C<sub>6</sub>H<sub>5</sub>), 221.89 (cis-CO), 227.40 (trans-CO); highresolution ESIng-MS (MeCN) found 591.0796 (calc 591.0820 dev: -4.1 ppm); IR  $(CH_2Cl_2) \nu$  1887 (s) (CO), 1923 (s) (CO), 2006 (s) (CO) cm<sup>-1</sup>. Anal. Calcd for C<sub>31</sub>H<sub>27</sub>CrNO<sub>4</sub>P<sub>2</sub> (found): C, 62.95 (62.93); H, 4.60 (4.56); N, 2.37 (2.31).

Synthesis of Ag[Al(OC(CF<sub>3</sub>)<sub>3</sub>)<sub>4</sub>]. LiAlH<sub>4</sub> (1.0g, 0.026 mol) was suspended in hexane (60 mL) and cooled to 253 K, and HOC(CF<sub>3</sub>)<sub>3</sub> (15 mL, 0.11 mol) was added slowly. The mixture was stirred for 45 min, then heated under reflux overnight using a condenser set at 253 K. The solution was filtered, the product washed with hexane, and solvent removed *in vacuo* to yield the white solid Li[Al(OC(CF<sub>3</sub>)<sub>3</sub>)<sub>4</sub>] (20.0g, 80%): <sup>19</sup>F NMR ((CD<sub>3</sub>)<sub>2</sub>SO, 250 MHz, 298 K)  $\delta$  (ppm) –75.06. Li[Al(OC(CF<sub>3</sub>)<sub>3</sub>)<sub>4</sub>] (10.0 g, 0.01 mol) and AgF (1.7g, 0.013 mol) were suspended in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) in the dark and mixed in an ultrasonic bath overnight. The solution was filtered, and the solvent removed *in vacuo* to yield the white solid Ag[Al(OC(CF<sub>3</sub>)<sub>3</sub>)<sub>4</sub>] (8.3g, 77%).

Synthesis of Cr(I) Tetracarbonyl Species [Cr(CO)<sub>4</sub>(Ph<sub>2</sub>PN-(*i*Pr)PPh<sub>2</sub>][Al(OC(CF<sub>3</sub>)<sub>3</sub>)<sub>4</sub>]. Cr(0)1 (100 mg, 0.17 mmol) and Ag[Al(OC(CF<sub>3</sub>)<sub>3</sub>)<sub>4</sub>] (220 mg, 0.23 mmol) were dissolved in dichloromethane (5 mL) to give a dark blue solution. The Schlenk tube was covered with foil to reduce exposure of the reaction mixture to light. The solution was stirred at room temperature overnight, then filtered, and the solvent removed *in vacuo* to yield the blue solid [Cr(CO)<sub>4</sub>(Ph<sub>2</sub>PN(*i*Pr)PPh<sub>2</sub>)][Al(OC(CF<sub>3</sub>)<sub>3</sub>)<sub>4</sub>]: dark blue powder (105 mg, 40%); high-resolution ESI<sub>pos</sub>-MS (MeCN) found 591.0824 (calc 591.0820 dev: 0.6 ppm); IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$  1962 (s)(CO), 2032 (s)(CO), 2086 (s)(CO) cm<sup>-1</sup>; <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, 282 MHz)  $\delta$ (ppm) -76.2 (s,  $\Delta \nu_{1/2}$  = 8.41 Hz). Anal. Calcd for C<sub>47</sub>H<sub>27</sub>AlCrF<sub>36</sub>NO<sub>8</sub>P<sub>2</sub> (found): C, 36.22 (36.19); H, 1.75 (1.77); N, 090 (0.99).

**Sample Preparation for EPR Measurements.**  $[Cr(CO)_41]^+$  (6 mg of the solid containing the Ag[Al(OC(CF<sub>3</sub>)<sub>3</sub>)<sub>4</sub>] counterion) was dissolved in 200  $\mu$ L of dichloromethane in the EPR tube under anaerobic conditions (1.92 × 10<sup>-2</sup> M). Triethylaluminum (predissolved in hexane or dichloromethane; 0.1 M) was added directly to the solution using a microsyringe. A sufficient quantity was delivered to the tube, affording different TEA:Cr molar ratios of between 2 and 10 equiv. The TEA was added to the precooled EPR tube containing the [Cr(CO)<sub>4</sub>1]<sup>+</sup> solution (at either 298 or 273 K). The samples were frozen immediately to 77 K by immersing in liquid nitrogen. The

frozen solution CW EPR spectra were recorded at 140 K. The samples were then slowly and progressively annealed at increasing temperatures (i.e., 200, 273, and 298 K, overnight), allowing the intermediate  $[Cr(CO)_{r}1]^{+}$  species to be detected.

**Details of DFT Calculations.** Geometry was optimized using Turbomole<sup>26</sup> at the uBP86/def2-TZVP level<sup>27,28</sup> and confirmed as a true minimum via harmonic frequency calculation. Hyperfine coupling and g tensor data were calculated in ORCA  $2.8^{29}$  using the hybrid PBE0 functional<sup>30</sup> and a basis set consisting of EPR-II on C and H,<sup>31</sup> def2-TZVP on P,<sup>28</sup> and the "Core Properties" basis (defined in ORCA for first-row transition metals) on Cr.<sup>3</sup>

# AUTHOR INFORMATION

# **Corresponding Author**

\*E-mail: cartere4@cf.ac.uk; cavellkj@cf.ac.uk; murphydm@cf. ac.uk.

#### Notes

The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

L.M. acknowledges funding from SASOL. EPSRC funding (EP/H023879) is also gratefully acknowledged.

### REFERENCES

(1) (a) Dixon, J. T.; Green, M. J.; Hess, F. M.; Morgan, D. H. J. Organomet. Chem. 2004, 689, 3641. (b) McGuinness, D. S. Chem. Rev. 2011, 111, 2321.

(2) (a) McGuinness, D. S.; Wasserscheid, P.; Keim, W.; Hu, C.; Englert, U.; Dixon, J. T.; Grove, J. J. C. Chem. Commun. 2003, 334. (b) McGuinness, D. S.; Wasserscheid, P.; Keim, W.; Morgan, D.; Dixon, J. T.; Bollmann, A.; Maumela, H.; Hess, F.; Englert, U. J. Am. Chem. Soc. 2003, 125, 5272. (c) Dixon, J. T.; Wasserscheid, P.; McGuinness, D. S.; Hess, F. M.; Maumela, H.; Morgan, D. H.; Bollmann, A. WO 03053890A1, 2003 (Sasol Technology). (d) McGuinness, D. S.; Wasserscheid, P.; Morgan, D. H.; Dixon, J. T. Organometallics 2005, 24, 552. (e) McGuinness, D. S.; Brown, D. B.; Tooze, R. P.; Hess, F. M.; Dixon, J. T.; Slawin, A. M. Z. Organometallics 2006, 25, 3605.

(3) (a) Jabri, A.; Temple, C.; Crewdson, P.; Gambarotta, S.; Korobkov, I.; Duchateau, R. J. Am. Chem. Soc. 2006, 128, 9238. (b) Temple, C.; Jabri, A.; Crewdson, P.; Gambarotta, S.; Korobkov, I.; Duchateau, R. Angew. Chem. 2006, 118, 7208.

(4) (a) Carter, A.; Cohen, S. A.; Cooley, N. A.; Murphy, A.; Scutt, J.; Wass, D. F. Chem. Commun. 2002, 858. (b) Wass, D. F. Dalton Trans. 2007, 816. (c) Overett, M. J.; Blann, K.; Bollmann, A.; Dixon, J. T.; Hess, F. M.; Killian, E.; Maumela, H.; Morgan, D. H.; Neveling, A.; Otto, S. Chem. Commun. 2005, 622. (d) Overett, M. J.; Blann, K.; Bollmann, A.; Dixon, J. T.; Hess, F.; Killian, E.; Maumela, H.; Morgan, D. H.; Neveling, A.; Otto, S. Chem. Commun. 2005, 622. (e) Agapie, T.; Day, M. W.; Henling, L. M.; Labinger, J. A.; Bercaw, J. E. Organometallics 2006, 25, 2733.

(5) Peitz, S.; Peulecke, N.; Aluri, B. R.; Muller, B. H.; Spannenberg, A.; Rosenthal, U.; Al-Hazmi, M. H.; Mosa, F. M.; Wohl, A.; Muller, W. Chem.-Eur. J. 2010, 16, 12127.

(6) (a) Yu, Z.; Houk, K. N. Angew. Chem., Int. Ed. 2003, 42, 808. (b) Kohn, R. D.; Smith, D.; Mahon, M. F.; Prinz, M.; Mihan, S.; Kociok-Kohn, G. J. Organomet. Chem. 2003, 683, 200-208. (c) Janse van Rensburg, W.; Van der Berg, J.-A.; Steynberg, P. J. Organometallics 2007, 26, 1000.

(7) (a) Zhang, J.; Li, A.; Andy Hor, T. S. Organometallics 2009, 28, 2935. (b) Jabri, A.; Mason, C. B.; Sim, Y.; Gambarotta, S.; Burchell, T. J.; Duchateau, R. Angew. Chem. 2008, 47, 9717.

(8) Chen, E. Y.-X.; Marks, T. J. Chem. Rev. 2000, 100, 1391.

(9) Bollmann, A.; Blann, K.; Dixon, J. T.; Hess, F. M.; Killian, E.; Maumela, H.; McGuinness, D. S.; Morgan, D. H.; Neveling, A.; Otto, S.; Overett, M.; Slawin, A. M. Z.; Wasserscheid, P.; Kuhlmann, S. J. Am. Chem. Soc. 2004, 126, 14712.

(10) Janse van Rensburg, W.; Grove, C.; Steynberg, J. P.; Stark, K. B.; Huyser, J. J.; Steynberg, P. J. Organometallics 2004, 23, 1207.

(11) Vidyaratne, L.; Nikiforov, G. B.; Gorelsky, S. L.; Gambarotta, S.; Duchateau, R.; Korobkov, I. Angew. Chem., Int. Ed. 2009, 48, 6552.

(12) Bowen, L. E.; Haddow, M. F.; Orpen, A. G.; Wass, D. F. Dalton Trans. 2007, 1160.

(13) McDyre, L. E.; Hamilton, T.; Murphy, D. M.; Cavell, K. J.; Gabrielli, W. F.; Hanton, M. J.; Smith, D. M. Dalton Trans. 2010, 39, 7792.

(14) McDyre, L. E.; Carter, E.; Cavell, K. J.; Murphy, D. M.; Platts, J. A.; Sampford, K.; Ward, B. D.; Gabrielli, W. F.; Hanton, M. J.; Smith, D. M. Organometallics 2011, 30, 4505.

(15) Rieger, P. H. Coord. Chem. Rev. 1994, 135, 203.

(16) For spin quantification analysis, both EPR spectra in Figure 1 (of  $[Cr(CO)_41]^{\dagger}$  and  $[Cr(1-bis-\eta^6-arene)]^+$ ) were recorded at the same temperature (140 K) and power (5 mW).

(17) Neese, F. Coord. Chem. Rev. 2009, 253, 526.

(18) (a) Rieger, A. L.; Rieger, P. H. Organometallics 2002, 21, 5868. (b) Cummings, D. A.; McMaster, J.; Rieger, A. L.; Rieger, P. H. Organometallics 1997, 16, 4362.

(19) (a) Li, T. T.; Kung, W.; Ward, D. L.; McCulloch, B.; Brubaker, C. H., Jr. Organometallics 1982, 1, 1229. (b) Prins, R.; Reinders, F. J. Chem. Phys. Lett. 1969, 3, 45. (c) Elschenbroich, C.; Kroker, J.; Massa, W.; Wunsch, M.; Ashe, A. J. Angew. Chem. 1986, 25, 571. (d) Elschenbroich, C.; Heikenfeld, G.; Wunsch, M.; Massa, W.; Baum, G. Angew. Chem. 1988, 27, 414. (e) Elschenbroich, C.; Sebbach, J.; Metz, B.; Heikenfeld, G. J. Organomet. Chem. 1992, 426, 173.

(20) (a) Connelly, N. G.; Orpen, A. G.; Rieger, A. L.; Rieger, P. H.; Scott, C. J.; Rosair, G. M. J. Chem. Soc., Chem. Commun. 1992, 1293. (b) Adams, C. J.; Bartlett, I. M.; Connelly, N. G.; Harding, D. J.; Hayward, O. D.; Martin, A. J.; Orpen, A. G.; Quayle, M. J.; Rieger, P. H. J. Chem. Soc., Dalton Trans. 2002, 4281. (c) Hammack, D. J.; Dillard, M. M.; Castellani, M. P.; Rheingold, A. L.; Rieger, A. L.; Rieger, P. H. Organometallics 1996, 15, 4791. (d) Castellani, M. P.; Connelly, N. G.; Pike, R. D.; Rieger, A. L.; Rieger, P. H. Organometallics 1997, 16, 4369. (e) Krusic, P. J.; McLain, S. J.; Morton, J. R.; Preston, K. F.; LePage, Y. J. Magn. Reson. 1987, 74, 72. (f) Morton, J. R.; McLain, S. J.; Cooley, N. A.; Baird, M. C.; Krusic, P. J.; McLain, S. J. J. Chem. Soc., Faraday Trans. 1 1987, 83, 3535.

(21) (a) Elschenbroich, C.; Stohler, F. Angew. Chem. 1975, 14, 174. (b) Clarke, G. R.; Clark, P. W. J. Organomet. Chem. 1983, 225, 205. (22) Balakrishna, M. S.; Prakasha, T. K.; Krishnamurthy, S. S. J.

Organomet. Chem. 1990, 390, 203.

(23) Rucklidge, A. J.; McGuinness, D. S.; Tooze, R. P.; Slawin, A. M. Z.; Pelletier, J. D. A.; Hanton, M. J.; Webb, P. B. Organometallics 2007, 26, 2782.

(24) Krossing, I.; Reisinger, A. Coord. Chem. Rev. 2006, 250, 2721.

(25) Spalek, T. P. P.; Sojka, Z. J. Chem. Inf. Model. 2005, 45, 18.

(26) Ahlrichs, R.; Bar, M.; Haser, M.; Horn, H.; Kolmel, C. Chem. Phys. Lett. 1989, 162, 165.

(27) (a) Becke, A. D. Phys. Rev. A 1998, 38, 3098. (b) Perdew, J. P. Phys. Rev. B 1986, 33, 8822.

(28) Weigend, F.; Ahlrichs, R. Phys. Chem. Chem. Phys. 2005, 7, 3297.

(29) (a) Neese, F. J. Chem. Phys. 2001, 115, 11080. (b) Neese, F. J.

Phys. Chem. A 2001, 105, 4290. (c) Neese, F. J. Chem. Phys. 2003, 118,

3939. (d) Neese, F. J. Chem. Phys. 2005, 122, 34107(1).

(30) Adamo, C.; Barone, V. J. Chem. Phys. 1996, 110, 6158.

(31) Barone, V. In Recent Advances in Density Functional Methods, Part I; Chong, D. P., Ed.; World Scientific Publ. Co.: Singapore, 1996.

(32) The ORCA basis set "CoreProp" was used. This basis is based on the TurboMole DZ basis developed by Ahlrichs and co-workers and obtained from the basis set library under ftp.chemie.uni-karlsruhe. de/pub/basen.

н