

Organometallic Chemistry of Chromium(VI): Synthesis of Chromium(VI) Alkyls and Their Precursors. X-ray Crystal Structure of the Metallacycle $\text{Cr}(\text{N}^t\text{Bu})_2\{o\text{-(CHSiMe}_3)_2\text{C}_6\text{H}_4\}$

Nicolaas Meijboom and Colin J. Schaverien*

Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research B.V.), P.O. Box 3003, 1003 AA Amsterdam, The Netherlands

A. Guy Orpen

Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS, U.K.

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Reaction of $\text{Cr}(\text{N}^t\text{Bu})_2(\text{OSiMe}_3)_2$ (1) with Me_3SiBr in the presence of 1 equiv of pyridine affords $\text{Cr}(\text{N}^t\text{Bu})_2(\text{py})\text{Br}_2$ (2), which provides a convenient entry into the chemistry of chromium(VI) alkyl complexes. The chloride analogue $\text{Cr}(\text{N}^t\text{Bu})_2(\text{py})\text{Cl}_2$ (4) can be prepared from 1 and ethereal HCl, followed by addition of pyridine. Treatment of 1 with H_2O (2 equiv) affords $\text{Cr}(\text{O})(\text{N}^t\text{Bu})_2(\text{OSiMe}_3)_2$ (6) in high yield. 6 reacts with PCl_5 to give $\text{Cr}(\text{O})(\text{N}^t\text{Bu})\text{Cl}_2$. Alkylation of 2 and 4 with $\text{Me}_3\text{SiCH}_2\text{MgCl}$, $\text{Zn}(\text{CH}_2\text{CMe}_3)_2$, or $\text{PhCMe}_2\text{CH}_2\text{MgCl}$ affords the corresponding dialkyl species $\text{Cr}(\text{N}^t\text{Bu})_2(\text{CH}_2\text{SiMe}_3)_2$ (7), $\text{Cr}(\text{N}^t\text{Bu})_2(\text{CH}_2\text{CMe}_3)_2$ (8), and $\text{Cr}(\text{N}^t\text{Bu})_2(\text{CH}_2\text{CMe}_2\text{Ph})_2$ (9) respectively, as dark red oils. Reaction of 2 with the sterically hindered dilithium reagent $o\text{-C}_6\text{H}_4\{(\text{CHSiMe}_3)\text{Li}(\text{TMEDA})\}_2$ affords crystalline $\text{Cr}(\text{N}^t\text{Bu})_2\{o\text{-(CHSiMe}_3)_2\text{C}_6\text{H}_4\}$ (10), the X-ray crystal structure of which has been determined. 10 crystallizes in the monoclinic system $P2_1/c$, with $a = 9.710$ (3) Å, $b = 29.959$ (9) Å, $c = 10.149$ (3) Å, $\beta = 110.40$ (2)°, $V = 2767.0$ (13) Å³, and $Z = 4$. Reaction of 2 with $\text{Mg}(\text{C}_5\text{H}_5)_2(\text{THF})_{2.5}$ affords $\text{Cr}(\text{C}_5\text{H}_5)(\text{N}^t\text{Bu})_2\text{Br}$, which can be converted into the monoalkyl species $\text{Cr}(\text{C}_5\text{H}_5)(\text{N}^t\text{Bu})_2\text{R}$ ($\text{R} = \text{Me}, \text{CH}_2\text{SiMe}_3, \text{CH}_2\text{CMe}_3, \text{CH}_2\text{CMe}_2\text{Ph}$).

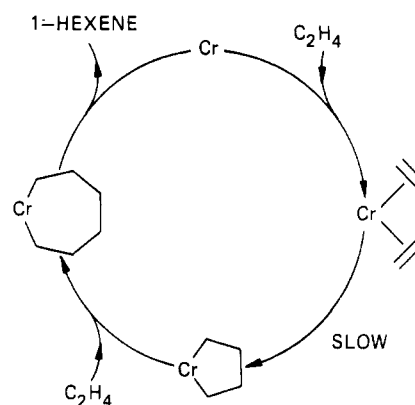
Introduction

Chromium-based catalysts are currently used to manufacture high-density polyethylene by using a dispersion of Cr(III-VI) sites bound to a silica support.^{1,2} Cr(III) stearate/aluminum alkyl/magnesium chloride systems produce high molecular weight polyethylene with narrow dispersities.^{3,4} Significantly, the selective trimerization of ethylene to 1-hexene using a homogeneous chromium catalyst has been recently reported.⁵

It is probable that polymerization proceeds via a conventional metal-alkyl insertion pathway. Indeed, well-characterized, low-valent chromium species have been shown to be active for the polymerization of olefins, albeit at relatively modest rates. For example, $\text{CrRCl}_2(\text{THF})_3$ ($\text{R} = \text{Me}, \text{Et}$) is active for ethylene polymerization, and Theopold⁷ has demonstrated that $[\text{Cr}(\text{C}_5\text{Me}_5)\text{Me}(\text{THF})_2]\text{BPh}_4$ slowly polymerizes ethylene and propylene.

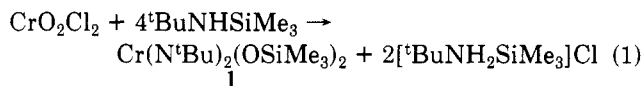
In contrast, trimerization of ethylene to 1-hexene (Scheme I) could be associated with a high-valent metallacyclic pathway. By this proposed⁵ metallacycle route, two molecules of ethylene coordinated to a chromium(III) species rearrange to a high-valent chroma(V)cyclopentane, which reacts with a third equivalent of ethylene to give an unstable chromacycloheptane. This putative species yields, by β -hydrogen elimination/reductive elimination, the original chromium(III) catalyst and 1-hexene.

Scheme I. Proposed Pathway for the Selective Trimerization of Ethylene



We wished to demonstrate that such high-valent chromium alkyl and metallacycle species were realistic entities.

There is a remarkable dearth of precursors with which to gain an entry into the chemistry of chromium in high oxidation states. There also exists many inherent synthetic difficulties associated with their oxidizing properties. For example, CrO_2Cl_2 is a volatile red liquid that attacks silicon grease, fumes vigorously on exposure to moist air, and exothermically oxidizes toluene. The oxidizing power of CrO_2Cl_2 can be effectively suppressed by replacing the oxo ligands with the isoelectronic but sterically more protective imido ligand⁸ (eq 1). Organoimido species⁹ are ideally



suited for a study of metal-carbon bonds because their ability for variable electron donation and their strength of π -bonding facilitates stabilization of metals in high oxidation states.

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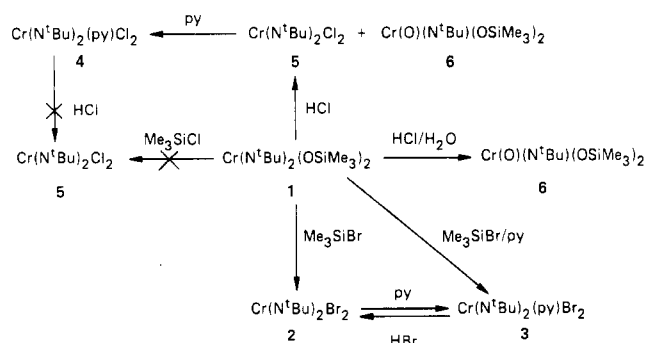
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Scheme II

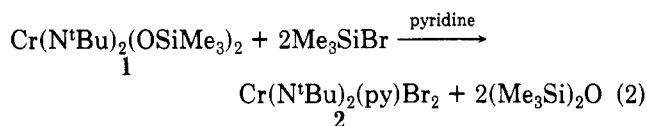


To the best of our knowledge no Cr(VI) alkyl species have previously been reported although the protected aryl derivatives $\text{Cr}(\text{N}^t\text{Bu})_2(2,4,6\text{-C}_6\text{H}_2\text{Me}_3)_2$ and $\text{Cr}(\text{N}^t\text{Bu})_2(2,6\text{-C}_6\text{H}_3\text{Me}_2)_2$ have been synthesized¹⁰ by reaction of the appropriate Grignard reagent with 1. In contrast, alkylation of 1 with ZnPh_2 gave biphenyl and $^t\text{BuNHPH}$ as the only identifiable products.¹¹ In related W(VI) and Mo(VI) chemistry, reaction of $\text{W}(\text{N}^t\text{Bu})_2(\text{O}^t\text{Bu})_2$ and $\text{Mo}(\text{N}^t\text{Bu})_2(\text{OSiMe}_3)_2$ with Me_2Zn gave the dimethyl dimers $[\text{M}(\text{N}^t\text{Bu})_2\text{Me}_2]_2$ ($\text{M} = \text{Mo},^{11} \text{W}^{12}$), but no analogous reaction has been described for the chromium complex.

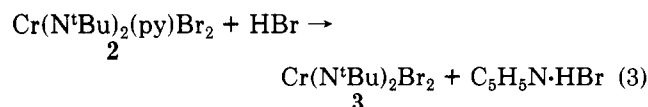
Results and Discussion

Synthesis of Starting Materials. The preparation of bisalkyl species using 1 as precursor was unsuccessful. Reaction of 1 with alkylmagnesium or alkyllithium reagents, under various conditions, gave a mixture of reduced paramagnetic products. Furthermore, $\text{Cr}(\text{N}^t\text{Bu})_2(\text{CH}_2\text{CMe}_3)_2$ could not be synthesized cleanly by using a milder alkylating agent such as $\text{Zn}(\text{CH}_2\text{CMe}_3)_2$, which might have been expected to circumvent problems associated with reduction. We consequently sought a new Cr(VI) precursor in order to facilitate entry into Cr(VI) alkyl chemistry. The results presented in this section are summarized in Scheme II.

Fortunately, 1 can be converted to a suitable starting material by reaction with 2 equiv of trimethylsilyl bromide in the presence of a small excess of pyridine to afford $\text{Cr}(\text{N}^t\text{Bu})_2(\text{py})\text{Br}_2$ (2) in 90% yield (eq 2).

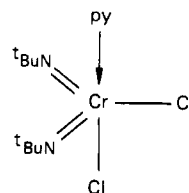


This reaction can be readily performed on a 20-g scale. The use of pyridine is advantageous as it enables $\text{Cr}(\text{N}^t\text{Bu})_2(\text{py})\text{Br}_2$ (2) to be conveniently isolated as an orange, crystalline, hexane-insoluble powder. Although the reaction can be performed without pyridine, the product $\text{Cr}(\text{N}^t\text{Bu})_2\text{Br}_2$ (3) is an extremely hexane-soluble purple oil, which hinders purification. The preferred method of synthesis of 3 is by reaction of 2 with HBr in ether (eq 3).



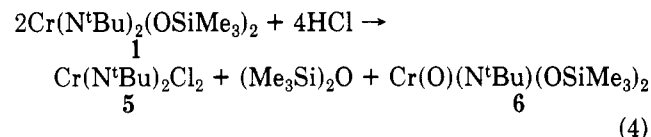
The two imido ligands in five-coordinate $\text{Cr}(\text{N}^t\text{Bu})_2(\text{py})\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$) presumably adopt a mutually cisoid

orientation to minimize competition for the available d orbitals and maximize π -bonding with the chromium. We assume that the following geometry is adopted, by analogy to that found for $\text{W}(\text{O})(\text{CH}^t\text{Bu})\text{Cl}_2(\text{PET}_3)$.¹³

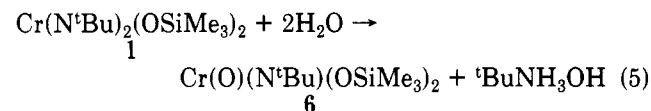


At this juncture, it is not known if $\text{Cr}(\text{N}^t\text{Bu})_2\text{Br}_2$ (3) and $\text{Cr}(\text{N}^t\text{Bu})_2\text{Cl}_2$ (5, *vide infra*) are monomers or are dimers with halide bridges. Attempts at removing an imido group from 3, by further protonation using excess HBr, were unsuccessful.

In contrast, $\text{Cr}(\text{N}^t\text{Bu})_2(\text{py})\text{Cl}_2$ (4) cannot be prepared by reaction of 1 with Me_3SiCl ; however, treatment of 1 with ethereal HCl affords $\text{Cr}(\text{N}^t\text{Bu})_2\text{Cl}_2$ (5) as a purple oil in ca. 50% yield. The other product of this reaction is the previously reported⁸ monoimido species $\text{Cr}(\text{O})(\text{N}^t\text{Bu})(\text{OSiMe}_3)_2$ (6), also in ca. 50% yield. These two oils can be easily separated by addition of pyridine to a hexane solution of the crude reaction mixture to precipitate $\text{Cr}(\text{N}^t\text{Bu})_2(\text{py})\text{Cl}_2$ (4) as a pure, orange crystalline solid leaving 6 in solution (eq 4).



We assume that $\text{Cr}(\text{O})(\text{N}^t\text{Bu})(\text{OSiMe}_3)_2$ is formed from the equivalent of water that is produced on condensation of Me_3SiOH to $(\text{Me}_3\text{Si})_2\text{O}$. Indeed, addition of water (2 equiv) to an ether solution of $\text{Cr}(\text{N}^t\text{Bu})_2(\text{OSiMe}_3)_2$ at -78°C results in the clean formation of 6 (eq 5).



Two equivalents of water are required because liberated $^t\text{BuNH}_2$ is rapidly protonated by unreacted H_2O to precipitate $^t\text{BuNH}_3\text{OH}$. In agreement with this, simultaneous addition of 1 equiv of H_2O and 1 equiv of ethereal HCl resulted in a cleaner reaction to give 6 and $^t\text{BuNH}_3\text{Cl}$. This is a simpler and more straightforward preparation than that previously described,⁸ which involved treatment of 1 with 1 equiv of benzaldehyde (toluene, 70°C , 16 h), followed by addition of $\text{CF}_3\text{SO}_3\text{Me}$ in order to separate $\text{Cr}(\text{O})(\text{N}^t\text{Bu})(\text{OSiMe}_3)_2$ (6) from the imine by conversion of the latter to the insoluble salt $[\text{PhCH}=\text{NMe}^t\text{Bu}]\text{SO}_3\text{CF}_3$. Addition of H_2O (1 equiv) to $\text{V}(\text{NC}_6\text{H}_4\text{Me})(\text{O}-2,6\text{-C}_6\text{H}_3\text{Me}_2)_3$ has been reported to result in hydrolysis to $\text{V}(\text{O})(\text{O}-2,6\text{-C}_6\text{H}_3\text{Me}_2)_3$ and $p\text{-MeC}_6\text{H}_4\text{NH}_2$.¹⁴

To prepare potentially more reactive monoimido-chromium(VI) precursors, we postulated that treatment of $\text{Cr}(\text{O})(\text{N}^t\text{Bu})(\text{OSiMe}_3)_2$ with PCl_5 would replace the oxo ligand by two chlorides to afford $\text{Cr}(\text{N}^t\text{Bu})\text{Cl}_2(\text{OSiMe}_3)_2$. Encouragingly, ^{31}P NMR monitoring of the reaction mix-

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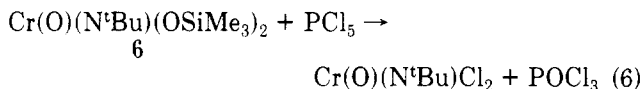
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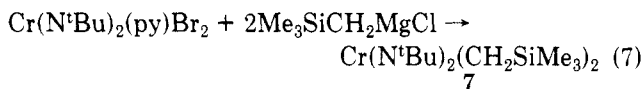
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ture indicated formation of POCl_3 . Instead a purple oil was isolated that possessed just one ^1H NMR resonance (δ 1.17 in C_6D_6), the elemental analysis of which indicated formation of $\text{Cr}(\text{O})(\text{N}^t\text{Bu})\text{Cl}_2$ (eq 6). The fate of the trimethyl siloxide groups, as either Me_3SiCl or $(\text{Me}_3\text{Si})_2\text{O}$, was not determined.



It was hoped that the controlled reduction of the dihalides **2** and **4** under an ethylene atmosphere would lead to metallacycle formation. This failed to give either isolable species or formation of 1-hexene.

Synthesis of Alkyl Complexes. In contrast to $\text{Cr}(\text{N}^t\text{Bu})_2(\text{OSiMe}_3)_2$ (**1**), $\text{Cr}(\text{N}^t\text{Bu})_2(\text{py})\text{Br}_2$ (**2**) can be cleanly alkylated with judiciously chosen reagents (eq 7). Reaction of **2** with $\text{Me}_3\text{SiCH}_2\text{MgCl}$ afforded the first $\text{Cr}(\text{VI})$ alkyl complex.



The choice of alkylating reagent is clearly critical in order to prevent reduction. It is essential that the alkylation step be designed to give a very clean product, as it is not possible to purify these extremely soluble oils by recrystallization. Although reaction of **2** with neopentylmagnesium or dineopentylmagnesium gave the chromium dineopentyl compound $\text{Cr}(\text{N}^t\text{Bu})_2(\text{CH}_2\text{CMe}_3)_2$ (**8**), it could not be purified sufficiently. Reaction of **4** with dineopentylzinc afforded pure **8**. $\text{Cr}(\text{N}^t\text{Bu})_2(\text{CH}_2\text{CMe}_2\text{Ph})_2$ (**9**) was obtained from reaction of **2** with $\text{PhCMe}_2\text{CH}_2\text{MgCl}$ in toluene. These chromium alkyl compounds are very soluble, dark red oils which were characterized by ^1H and ^{13}C NMR spectroscopy (Table I) and elemental analysis.

It was not possible to prepare the dimethyl species $\text{Cr}(\text{N}^t\text{Bu})_2\text{Me}_2$ by reaction of **2** with MeLi , MeMgI , MgMe_2 , or SnMe_4 , although ^1H NMR spectra of the crude, red oily product revealed signals that could be attributed to $\text{Cr}(\text{N}^t\text{Bu})_2\text{Me}_2$; however, it could not be isolated pure.

It is notable that the coordinated pyridine from **2** and **4** is not retained in the dialkyl species, presumably reflecting the increased steric congestion around chromium. We have been unable to prepare compounds of the type $\text{Cr}(\text{N}^t\text{Bu})_2\text{R}_2\text{L}$, even by treatment of $\text{Cr}(\text{N}^t\text{Bu})_2\text{R}_2$ with a strongly coordinating ligand such as PMe_3 .

The coordination sphere around chromium in $\text{Cr}(\text{N}^t\text{Bu})_2\text{R}_2$ is assumed to be pseudotetrahedral, since the protons of the α - CH_2 groups in compounds **7**–**9** are non-diastereotopic. Crystallographically characterized $\text{Cr}(\text{N}^t\text{Bu})_2(2,4,6\text{-C}_6\text{H}_2\text{Me}_3)_2$ has a tetrahedral geometry.¹⁰

There is no NMR evidence for agostic interactions between the α - CH_2 groups and the chromium. The CH_2 groups resonate at 60.5 ($^1J_{\text{CH}} = 117$ Hz), 87.5 (126 Hz), and 86.1 ppm (122 Hz) for compounds **7**–**9**, respectively. Although these 16-electron species might be expected to contain such interactions, theoretical calculations¹⁵ indicate that in a tetrahedral complex they are much less favored, especially with good π -donor imido ligands present. For example, there is no evidence for agostic interactions in tetrahedral, high-spin, 13-electron $\text{Mn}(\text{CH}_2\text{CMe}_2\text{Ph})_2(\text{PMe}_3)_2$.¹⁶ These calculations were recently substantiated by gas-phase electron diffraction on TiCl_3Me , which provided no evidence for a distorted methyl group geometry.¹⁷

Table I. NMR Data of $\text{Cr}(\text{N}^t\text{Bu})_2\text{X}_2$ in C_6D_6

X	^1H NMR	^{13}C NMR (H-coupled) ^a	
		N ^t Bu	X
1 OSiMe ₃	0.29 (s)	31.3 (q)	2.6 (q)
	1.32 (s, N ^t Bu)	77.9 (s)	
2 Br(py)	1.53 (s, N ^t Bu)	29.2 (q)	124.1 (py) 137.4 (py) 151.6 (py)
	6.46 (py)	80.7 (s)	
	6.71 (py)		
	8.94 (py)		
3 Br	1.18 (s, N ^t Bu)		122.9 (py) 136.2 (py) 149.0 (py)
	1.50 (s, N ^t Bu)	27.8 (q)	
4 Cl(py)	6.57 (py)	79.6 (s)	
	6.83 (py)		
	8.87 (py)		
5 Cl	1.13 (s, N ^t Bu)	30.0 (q) 82.7 (s)	2.0 (q, 118, SiMe ₃) 60.5 (t, 117, CrCH ₂)
7 CH ₂ SiMe ₃	0.23 (s, SiMe ₃)	31.9 (q, 127)	32.7 (q, 126, CMe ₃) 34.3 (s, CMe ₃) 87.5 (t, 126, CrCH ₂)
	1.35 (s, N ^t Bu)	72.6 (s)	
	1.69 (s, CH ₂)		
8 CH ₂ CMe ₃	1.23 (s, CMe ₃)	33.5 (q, 125)	40.9 (s, CMe ₂) 86.1 (t, 122, CrCH ₂) 125.4 (d) 126.3 (d) 128.2 (d) 152.5 (s)
	1.40 (s, N ^t Bu)	71.4 (s)	
	2.11 (s, CH ₂)		
9 CH ₂ CMe ₂ Ph	1.25 (s, N ^t Bu)	31.8 (q, 125)	1.8 (q, 118, SiMe ₃) 70.3 (d, 122, CrCH) 127.7 (d, 159, C ₆ H ₄) 131.4 (d, 157, C ₆ H ₄) 132.8 (s, CCHSiMe ₃)
	1.55 (s, CMe ₂)	71.7 (s)	
	2.11 (s, CH ₂)		
	7.20 (m, Ar H)		
	7.40 (m, Ar H)		
10	0.49 (s, SiMe ₃)	31.1 (q, 127)	1.8 (q, 118, SiMe ₃) 70.3 (d, 122, CrCH) 127.7 (d, 159, C ₆ H ₄) 131.4 (d, 157, C ₆ H ₄) 132.8 (s, CCHSiMe ₃)
	0.88 (s, N ^t Bu)	33.3 (q, 126)	
	0.99 (s, CrCH)	70.9 (s)	
	1.60 (s, N ^t Bu)	71.7 (s)	
	7.27 (m, Ar H)		
	7.68 (m, Ar H)		

^as = singlet, d = doublet, t = triplet, q = quartet, $^1J_{\text{C-H}}$ in parentheses.

Thus electron deficiency at the metal is not necessarily a sufficient prerequisite to systematically induce $\text{M}\cdots\text{H}\cdots\text{C}$ interactions.

These bisalkyl species appear to possess remarkable thermal stability. They do not undergo thermal (or ligand) induced α -hydrogen elimination reactions, presumably due to efficient electron donation from the two imido groups and their tetrahedral geometry. We note that no chromium(VI) alkylidene complexes have been prepared, despite the considerable wealth of tungsten and, to a lesser extent, molybdenum examples.¹³

Osborn¹⁸ has recently reported that treatment of $\text{Mo}(\text{N}^t\text{Bu})_2(\text{CH}_2\text{CMe}_3)_2$ with 2 equiv of $(\text{CF}_3)_2\text{CHOH}$ for 10 min in pentane afforded the neopentylidene complex $\text{Mo}(\text{N}^t\text{Bu})(\text{CHCMe}_3)\{\text{OCH}(\text{CF}_3)_2\}_2(\text{NH}_2^t\text{Bu})$ via protonation at an imido nitrogen atom. In attempting to prepare the first $\text{Cr}(\text{VI})$ alkylidene complex, we have also reacted $\text{Cr}(\text{N}^t\text{Bu})_2(\text{CH}_2\text{CMe}_3)_2$ (**8**) with 2 equiv of $(\text{CF}_3)_2\text{CHOH}$ in hexane. No reaction was observed even after 15 h at 25 °C, **8** being recovered unchanged. Refluxing in hexane for 1 h led to the partial decomposition of **8**. $\text{Cr}(\text{N}^t\text{Bu})_2(\text{CH}_2\text{CMe}_3)_2$ (**8**) is surprisingly resistant to protonation; no reaction occurred on addition of 2 equiv of ethereal HCl at -78 °C. This lack of reactivity can be rationalized by the imido ligands in **8** being better π -electron donors than in their molybdenum analogue [cf. $\Delta\delta$ for $\text{M}(\text{N}^t\text{Bu})_2(\text{CH}_2\text{CMe}_3)_2 = 37.9$ (Cr), 33.3 ppm (Mo)¹⁸], and consequently they may be insufficiently basic to be susceptible to protonation.

To circumvent synthetic problems associated with the oily nature of the alkyls $\text{Cr}(\text{N}^t\text{Bu})_2\text{R}_2$, we postulated that introduction of 2,6-diisopropylphenylimido groups would

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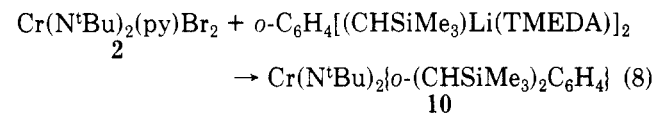
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offer considerable advantages because these compounds could be more crystalline and the 2,6-diisopropylphenylimido group would have less tendency to bridge two metal centers. Reaction of CrO_2Cl_2 or CrO_3 with ArNHSiMe_3 ($\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{Pr}_2$) in hexane or hexamethyldisiloxane under various conditions did not afford 2,6-diisopropylphenylimido products analogous to 1. Reaction of isocyanates with metal-oxo species is an established method¹⁹ of preparing the corresponding imido species with concomitant loss of CO_2 . Treatment of CrO_2Cl_2 with ArNCO (2 equiv, $-78 \rightarrow 25^\circ\text{C}$) or by refluxing in hexane or kerosene (bp 150°C) did not lead to a tractable product.

Preparation of Cr(VI) Metallacycles. We have demonstrated that it is possible to prepare dialkyl species based on the $\text{Cr}(\text{N}^t\text{Bu})_2$ fragment. Because of the possible involvement of chromacyclopentane species in the selective trimerization of ethylene, we wished to establish whether such metallacyclic compounds could be prepared to model this reaction. A crucial step in the formation of 1-hexene is the ring expansion reaction of a chromacyclopentane with ethylene to form an unstable chromacycloheptane. For selective trimerization, clearly ethylene insertion into the chromacyclopentane must be faster than elimination of 1-butene. However, we are unaware of any examples of olefin insertion into a simple metallacyclopentane. Platinacycloheptanes²⁰ have been shown to decompose by β -hydride elimination significantly faster than their smaller ring counterparts, the larger ring attaining the transition state necessary for β -hydride elimination. In view of our target of preparing unsubstituted high-valent chromium metallacycles we initially focused on the use of 1,4-dimagnesiobutane and 1,6-dimagnesiohexane²⁰ in order to prepare putative $\text{CrCH}_2(\text{CH}_2)_2\text{CH}_2(\text{N}^t\text{Bu})_2$ and $\text{CrCH}_2(\text{CH}_2)_4\text{CH}_2(\text{N}^t\text{Bu})_2$, respectively. Reaction of these di-Grignards with 2 in ether, benzene, or hexane/THF did not give isolable products. The reagent 1,4-dithio-2,2,3,3-tetramethylbutane²¹ would be expected to inhibit β -hydrogen decomposition pathways but did not react cleanly with 2. Because of the oily characteristics of the bisalkyl species 7-9 we proposed that incorporation of phenyl substituents or an aromatic ring into the metallacycle framework would reduce their high solubility and confer crystallinity on the resultant chromium metallacyclic species.

Reaction of 2 with the di-Grignards α,α' -dimagnesi-o-xylene or isolated, crystalline $o\text{-C}_6\text{H}_4(\text{CH}_2)_2\text{Mg}(\text{THF})_2$ ²² in ether, benzene, or hexane/THF did not afford isolable products. Use of a sterically more hindered precursor was successful.

Synthesis and Molecular Structure of $\text{Cr}(\text{N}^t\text{Bu})_2\{o\text{-(CHSiMe}_3)_2\text{C}_6\text{H}_4\}$. Reaction of $o\text{-C}_6\text{H}_4[(\text{CHSiMe}_3)\text{Li}(\text{TMEDA})_2]_2$ ²³ with 2 in ether affords $\text{Cr}(\text{N}^t\text{Bu})_2\{o\text{-(CHSiMe}_3)_2\text{C}_6\text{H}_4\}$ (10) in 64% isolated yield (eq 8).



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Table II. Bond Lengths (Å) for 10

Cr-N(1)	1.626 (4)	Cr-N(2)	1.651 (3)
Cr-C(1)	2.078 (4)	Cr-C(2)	2.368 (4)
Cr-C(3)	2.373 (4)	Cr-C(4)	2.076 (3)
Si(1)-C(1)	1.857 (4)	Si(1)-C(12)	1.864 (7)
Si(1)-C(13)	1.865 (6)	Si(1)-C(14)	1.855 (5)
Si(2)-C(4)	1.852 (4)	Si(2)-C(9)	1.859 (6)
Si(2)-C(10)	1.842 (5)	Si(2)-C(11)	1.853 (7)
N(1)-C(15)	1.456 (6)	N(2)-C(19)	1.435 (5)
C(1)-C(2)	1.464 (6)	C(2)-C(3)	1.438 (5)
C(2)-C(8)	1.426 (7)	C(3)-C(4)	1.463 (6)
C(3)-C(5)	1.423 (6)	C(5)-C(6)	1.361 (8)
C(6)-C(7)	1.384 (7)	C(7)-C(8)	1.367 (7)
C(15)-C(16)	1.506 (6)	C(15)-C(17)	1.514 (7)
C(15)-C(18)	1.532 (7)	C(19)-C(20)	1.415 (13)
C(19)-C(21)	1.356 (17)	C(19)-C(22)	1.443 (13)

Table III. Bond Angles (deg) for 10

N(1)-Cr-N(2)	114.6 (2)	N(1)-Cr-C(1)	108.9 (2)
N(2)-Cr-C(1)	116.1 (2)	N(1)-Cr-C(2)	144.0 (1)
N(2)-Cr-C(2)	97.2 (2)	C(1)-Cr-C(2)	37.7 (2)
N(1)-Cr-C(3)	143.4 (1)	N(2)-Cr-C(3)	97.2 (2)
C(1)-Cr-C(3)	68.9 (1)	C(2)-Cr-C(3)	35.3 (1)
N(1)-Cr-C(4)	108.3 (2)	N(2)-Cr-C(4)	115.7 (2)
C(1)-Cr-C(4)	90.6 (1)	C(2)-Cr-C(4)	68.9 (2)
C(3)-Cr-C(4)	37.7 (2)	C(1)-Si(1)-C(12)	107.3 (2)
C(1)-Si(1)-C(13)	110.1 (2)	C(12)-Si(1)-C(13)	107.2 (2)
C(1)-Si(1)-C(14)	112.0 (2)	C(12)-Si(1)-C(14)	110.4 (3)
C(13)-Si(1)-C(14)	109.6 (3)	C(4)-Si(2)-C(9)	110.7 (3)
C(4)-Si(2)-C(10)	112.1 (2)	C(9)-Si(2)-C(10)	109.1 (3)
C(4)-Si(2)-C(11)	107.8 (2)	C(9)-Si(2)-C(11)	107.0 (3)
C(10)-Si(2)-C(11)	110.1 (3)	Cr-N(1)-C(15)	171.2 (3)
Cr-N(2)-C(19)	155.8 (4)	Cr-C(1)-Si(1)	130.2 (2)
Cr-C(1)-C(2)	82.0 (2)	Si(1)-C(1)-C(2)	127.1 (3)
Cr-C(2)-C(1)	60.3 (2)	Cr-C(2)-C(3)	72.5 (2)
C(1)-C(2)-C(3)	121.2 (4)	Cr-C(2)-C(8)	135.3 (2)
C(1)-C(2)-C(8)	119.9 (3)	C(3)-C(2)-C(8)	118.0 (4)
Cr-C(3)-C(2)	72.2 (2)	Cr-C(3)-C(4)	60.1 (2)
C(2)-C(3)-C(4)	121.1 (4)	Cr-C(3)-C(5)	135.4 (3)
C(2)-C(3)-C(5)	117.3 (4)	C(4)-C(3)-C(5)	120.6 (4)
Cr-C(4)-Si(2)	128.2 (2)	Cr-C(4)-C(3)	82.3 (2)
Si(2)-C(4)-C(3)	126.8 (3)	C(3)-C(5)-C(6)	122.4 (4)
C(5)-C(6)-C(7)	120.3 (5)	C(6)-C(7)-C(8)	120.4 (5)
C(2)-C(8)-C(7)	121.6 (4)	N(1)-C(15)-C(16)	109.6 (4)
N(1)-C(15)-C(17)	107.5 (4)	C(16)-C(15)-C(17)	111.5 (4)
N(1)-C(15)-C(18)	108.6 (4)	C(16)-C(15)-C(18)	109.3 (4)
C(17)-C(15)-C(18)	110.2 (4)	N(2)-C(19)-C(20)	114.6 (5)
N(2)-C(19)-C(21)	111.6 (6)	C(20)-C(19)-C(21)	111.3 (9)
N(2)-C(19)-C(22)	109.2 (6)	C(20)-C(19)-C(22)	106.3 (8)
C(21)-C(19)-C(22)	103.0 (9)		

The ^1H NMR spectrum of 10 displays equivalent methyne and trimethylsilyl groups and inequivalent imido *tert*-butyl groups, as expected for the stereospecific formation of the meso isomer. This is consistent with both C_αH and C_βH protons being oriented toward one imido group and the xylenediyl ligand folded toward the other imido group. The meso isomer is the expected kinetically controlled product, as the $o\text{-C}_6\text{H}_4\text{C}_2$ fragment in $o\text{-C}_6\text{H}_4[(\text{CHSiMe}_3)\text{Li}(\text{TMEDA})_2]_2$ has been shown by X-ray crystallography to be planar.²⁴ The rac isomer may be thermodynamically unfavorable due to repulsive non-bonding interactions between the *tert*-butyl imido ligands and the bulky trimethylsilyl groups. The meso isomer was also observed in $\text{Zr}(\text{C}_5\text{H}_5)_2\{o\text{-(CHSiMe}_3)_2\text{C}_6\text{H}_4\}_2$ ²⁵ and in all other structurally characterized complexes containing this ligand.²⁵

The molecular structure shows a noncrystallographic mirror plane through the imido nitrogen and chromium

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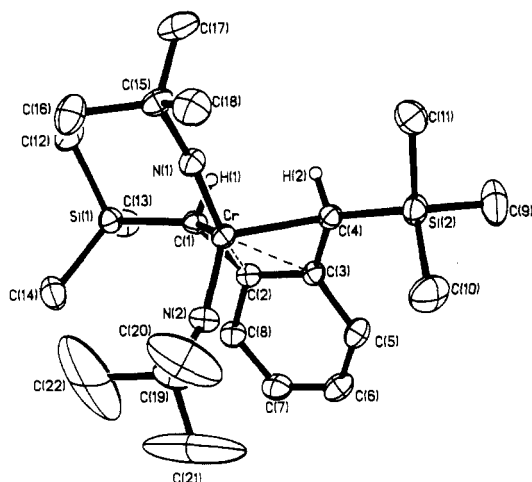


Figure 1. Molecular geometry of **10** with methyl and aryl group hydrogens omitted for clarity. Non-hydrogen atoms are drawn to enclose 20% probability density.

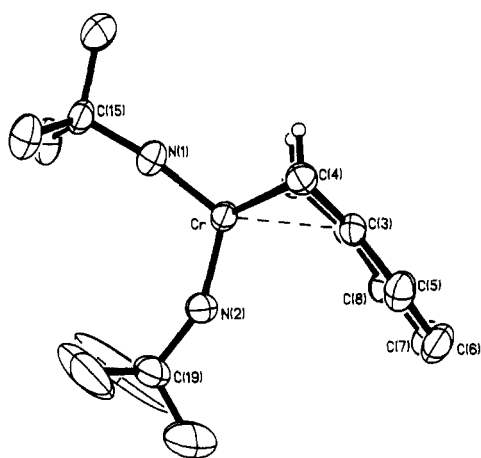


Figure 2. Molecular geometry of **10** with trimethylsilyl groups as well as aryl and methyl group hydrogen atoms omitted for clarity. Non-hydrogen atoms are drawn to enclose 30% probability density.

atoms. Bond lengths and angles are given in Tables II and III, with details of data collection and refinement listed in Table IV. Perspective views are given in Figures 1 and 2. The imido ligands are distorted from linearity at nitrogen, showing different deviations from 180° (Cr–N(1)–C(15) $171.2(3)^\circ$, Cr–N(2)–C(19) $155.8(3)^\circ$). The Cr–N distances show a corresponding variation (Cr–N(1) $1.636(4)$, Cr–N(2) $1.651(3)$ Å) with the more linear imido ligand showing the shorter Cr–N bond length, although both Cr–N distances are in the range appropriate for a triple Cr–N bond; cf. Cr–N bond lengths of 1.622 Å in Cr(N^tBu)₂(mesityl)₂,¹¹ 1.628 Å in Cr(N^tBu)₂[(CC₆H₂Me₃)=N^tBu]C₆H₂Me₃,¹¹ 1.562 Å in CrN(tetraphenylporphyrin),²⁶ and $1.65(1)$ Å in [Cr(C₅H₅)(NSiMe₃)(μ-NSiMe₃)₂].²⁷ It is therefore possible that one of the imido ligands is donating four and not six electrons; however, this difference may also be due to unfavorable repulsive interactions between the N(2)C(19)Me₃ imido and *o*-xylenediyl ligands. The only example²⁸ of a strongly bent imido ligand is in the bisimido complex Mo(NPh)₂(S₂CNET₂)₂, where the Mo–N–C angles are $139.4(4)$ and $169.4(4)^\circ$.

Table IV. Crystal Data and Data Collection Parameters for **10**

Crystal Data	
chem formula	C ₂₂ H ₄₂ N ₂ Cr
mol wt	442.8
cryst syst	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i> , No. 14
<i>a</i> , Å	9.710 (3)
<i>b</i> , Å	29.959 (9)
<i>c</i> , Å	10.149 (3)
β , deg	110.40 (2)
<i>V</i> , Å ³	2767.0 (13)
<i>Z</i>	4
<i>D</i> _{calcd} , g cm ⁻³	1.06
<i>F</i> (000), e	960
μ (Mo K α), cm ⁻¹	5.0
approx cryst dimen, mm	0.35 × 0.40 × 0.55
Data Collection	
check reflections	(4,15,-3), (6,6,-1), (265)
cryst decay during data collection, %	0
$\theta/2\theta$ range, deg	4.0 < 2θ < 50.0
scan method	Wyckoff ω
total data	4090
total unique data	3762
obsd <i>I</i> > 2 σ (<i>I</i>)	3252
Refinement	
no. of refined parameters	286
weighting factor <i>g</i>	0.0005
<i>R</i>	0.049
<i>R</i> _w	0.052
goodness of fit <i>S</i>	1.62
min/max residual densities in final Fourier map, e/Å ³	-0.31, 0.42
mean shift/esd in final cycle	0.05

The disubstituted *o*-xylenediyl ligand adopts a meso configuration and has the SiMe₃ groups in the sterically less hindered anti sites. The η^4 -binding of this ligand shows a pronounced distortion toward a chelating η^2 -form in which it would bind through atoms 1 and 4 only (Cr–C distances are 2.078 (4), 2.368 (4), 2.373 (4), and 2.076 (3) Å for atoms, 1, 2, 3, and 4, respectively). The fold angle between the [CrC(1)C(4)] and the [C(1)C(2)C(3)C(4)] planes is 67.1° . The interaction of one C–C bond of the arene ring with the chromium atom has a localizing effect on the C–C bonding of that ring (C–C bond lengths, 5–6, 6–7, and 7–8 are 1.361 (8), 1.384 (7), and 1.367 (7) Å, whereas C–C bond lengths 3–5, 2–3, and 2–8 are 1.423 (6), 1.438 (5), and 1.426 (7) Å, respectively). These structural characteristics resemble those observed in Zr(C₅H₅)₂{*o*-(CHSiMe₃)₂C₆H₄}₂,²⁵ for which the corresponding fold angle is 66.7° . This folding of the *o*-C₆H₄C₂ plane relative to the MC₂ plane has been observed in metallocycles of Zr(IV),²⁹ Nb(IV),²⁹ and W(VI)³⁰ containing the ligand [*o*-C₆H₄-(CH₂)₂]₂²⁻. The bis(xylenediyl) complex [W{*o*-(CH₂)₂C₆H₄O}Mg(THF)₄]₂²⁹ has fold angles of 66.1 and 42.4° , indicative of a π -interaction of just one xylenediyl ligand. The potential electronic unsaturation in the above compounds is presumably the driving force for the geometry adopted by the *o*-xylenediyl ligand, resulting in coordination of the arene π -bond. In contrast, the η^2 -*o*-xylenediyl unit is planar in 17-electron Mn(dmpe)₂{*o*-(CH₂)₂C₆H₄}₂,¹⁶ indicative of a solely diyl bonding mode. In general the ligand–metal bonding in **10** is best described as intermediate between that appropriate for chromium-

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(27) Wiberg, N.; Haring, H.-W.; Schubert, U. Z. *Naturforsch.* **1978**, *33B*, 1365.

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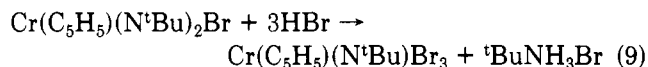
(29) Lappert, M. F.; Martin, T. R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1980**, 476. Lappert, M. F.; Martin, T. R.; Milne, C. R.; Atwood, J. L.; Hunter, W. E.; Pentilla, R. E. *J. Organomet. Chem.* **1980**, *192*, C35.

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(VI) metallacyclic and a chromium(IV) η^4 -diene structure. A structure involving η^4 -coordination of the *o*-xylenediyl ring to chromium with two 6-electron donor N^tBu^{2-} groups would give **10** an 18-electron count.

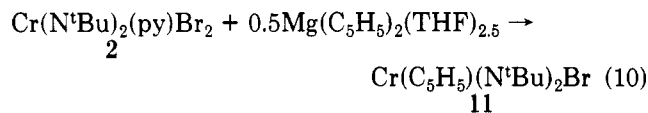
$\text{Cr}(\text{N}^t\text{Bu})_2\text{-}o\text{-(CHSiMe}_3)_2\text{C}_6\text{H}_4\text{}$ (**10**) did not react with ethylene; presumably the bulky substituents necessary to ensure its stability, also inhibit the insertion of ethylene.

Preparation of Cr(VI) Cyclopentadienyl Complexes. By introducing a cyclopentadienyl ligand, we hoped to synthesise more reactive monoimido species since the stabilizing influence of the cyclopentadienyl ligand should make an imido group susceptible to removal by protonation, as tBuNH_3Br (eq 9).

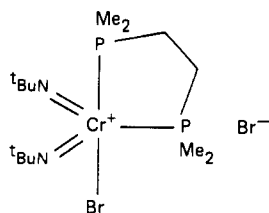


No monomeric Cr(VI) cyclopentadienyl species have been prepared, although the diamagnetic dimers $[\text{Cr}(\text{C}_5\text{H}_5)(\text{NSiMe}_3)(\mu\text{-NSiMe}_3)]_2$ ²⁷ and $[\text{Cr}(\text{C}_5\text{Me}_5)(\text{O})(\mu\text{-O})]_2$ ³¹ have been synthesized.

After much experimentation and use of a multitude of cyclopentadienyl reagents including $\text{C}_5\text{H}_5\text{MgCl}$, $\text{C}_5\text{H}_5\text{SnMe}_3$, $\text{C}_5\text{H}_5\text{SiMe}_3$, $\text{C}_5\text{H}_5\text{Ti}$, and $(\text{C}_5\text{H}_5)_2\text{Zn}$, the clean formation of $\text{Cr}(\text{C}_5\text{H}_5)(\text{N}^t\text{Bu})_2\text{Br}$ was finally achieved in good yield by use of $\text{Mg}(\text{C}_5\text{H}_5)_2(\text{THF})_{2.5}$ (eq 10). Com-



pound **11** is unstable in solution, and NMR monitoring of **11** in C_6D_6 indicates slow decomposition (days) to a new, but as yet, unidentified diamagnetic chromium product. $\text{Cr}(\text{C}_5\text{H}_5)(\text{N}^t\text{Bu})_2\text{Cl}$ (**12**), prepared from **4** and $\text{Mg}(\text{C}_5\text{H}_5)_2(\text{THF})_{2.5}$, is more stable in solution. In view of the formal 20-electron count for pseudooctahedral **11** and **12** (counting the cyclopentadienyl ligand as occupying three facial sites and N^tBu^{2-} as a 6-electron donor), they may contain a bent imido group or a slipped cyclopentadienyl ring as there are only three available d orbitals of π -symmetry to interact with the four π -donor orbitals of the two essentially sp-hybridized imido ligands. NMR spectra do not indicate any such asymmetric bonding mode. This formal 20-electron count is perhaps the cause of the labile nature of **11** and **12**. The mode of decomposition of **11** and **12** could be analogous to that of **18** (vide infra) by formation of ionic $[\text{Cr}(\text{C}_5\text{H}_5)(\text{N}^t\text{Bu})_2]\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$). We have shown that formation of a cationic Cr(VI) species is a route available to such compounds in order to relieve their formal 20-electron count. Treatment of $\text{Cr}(\text{N}^t\text{Bu})_2(\text{py})\text{Br}_2$ with 1,2-bis(dimethylphosphino)ethane, in toluene at -30°C gave $[\text{Cr}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)(\text{N}^t\text{Bu})_2\text{Br}]\text{Br}$ (**18**) as a bright yellow powder that is insoluble in toluene but readily soluble in CH_2Cl_2 . The stereochemistry of **18** is unknown but the equivalent *tert*-butylimido groups and the inequivalent dmpe resonances (see Experimental Section) suggest a trigonal bipyramid geometry:



(31) Herberhold, M.; Kremmitz, W.; Razavi, A.; Schollhorn, H.; Thewalt, U. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 601.

Table V. NMR Data for $\text{Cr}(\text{C}_5\text{H}_5)(\text{N}^t\text{Bu})_2\text{X}$ in C_6D_6

X	¹ H NMR	¹³ C NMR (H-coupled) ^a	
		$\text{N}^t\text{Bu}/\text{C}_5\text{H}_5$	X
11 Br	1.26 (s, N^tBu)	29.9 (q, 128)	
	5.93 (s, C_5H_5)	79.1 (s)	
		110.0 (d, 176)	
12 Cl	1.27 (s, N^tBu)		
	5.94 (s, C_5H_5)		
13 CH_3	1.19 (s, CH_3)	30.5 (q, 127)	2.5 (q, 136)
	1.22 (s, N^tBu)	73.3 (s)	
	5.71 (s, C_5H_5)	106.3 (d, 173)	
14 CH_2SiMe_3	0.34 (s, SiMe_3)	30.8 (q, 127)	3.0 (q, 118, SiMe_3)
	0.74 (s, CrCH_2)	73.7 (s)	6.1 (t, 121, CrCH_2)
	1.18 (s, N^tBu)	105.5 (d, 173)	
15 CH_2CMe_3	5.74 (s, C_5H_5)		
	1.20 (s, CMe_3)	31.1 (q, 127)	34.2 (q, 127, CMe_3)
	1.22 (s, N^tBu)	73.7 (s)	44.6 (t, 128, CrCH_2)
	2.64 (s, CrCH_2)	105.7 (d, 172)	
16 $\text{CH}_2\text{CMe}_2\text{-Ph}$	5.67 (s, C_5H_5)		
	1.22 (s, N^tBu)	31.0 (q, 125)	34.4 (q, 125, CMe_2)
	1.54 (s, Me_2)	73.8 (s)	40.3 (s, CMe_2)
	2.85 (s, CrCH_2)	105.3 (d, 173)	43.9 (t, 131, CrCH_2)
	5.50 (s, C_5H_5)		125.5 (d)
	7.30 (Ph)		126.6 (d)
	7.64 (Ph)		127.0 (d)
			153.3 (s)

Compounds **11** and **12** can be alkylated to give $\text{Cr}(\text{C}_5\text{H}_5)(\text{N}^t\text{Bu})_2\text{R}$ ($\text{R} = \text{Me}$ (**13**), CH_2CMe_3 (**14**), CH_2SiMe_3 (**15**), and $\text{CH}_2\text{CMe}_2\text{Ph}$ (**16**)) as extremely soluble, dark red oils. In contrast to **11** and **12**, these formally 20-electron species are stable in solution. Their ¹H and ¹³C NMR data are listed in Table V.

To circumvent the problems associated with the unstable starting materials **11** and **12**, a one-pot procedure beginning with **2** was employed, utilizing first $\text{Mg}(\text{C}_5\text{H}_5)_2(\text{THF})_{2.5}$, followed by the appropriate alkylating reagent to afford the monoalkyl product in ca. 80% yield.

Reaction of $\text{Cr}(\text{C}_5\text{H}_5)(\text{N}^t\text{Bu})_2\text{Br}$ with the hydride source LiEt_3BH did not afford putative $\text{Cr}(\text{C}_5\text{H}_5)(\text{N}^t\text{Bu})_2\text{H}$ but gave the diamagnetic imido-bridged dimer $[\text{Cr}(\text{C}_5\text{H}_5)(\text{N}^t\text{Bu})(\mu\text{-N}^t\text{Bu})]_2$ (**17**), which was identified by comparison of its ¹H and ¹³C NMR spectra with those of $[\text{Cr}(\text{C}_5\text{H}_5)(\text{NSiMe}_3)(\mu\text{-NSiMe}_3)]_2$.²⁷

All attempts to prepare a pentamethylcyclopentadienyl analogue of **8** by use of $\text{C}_5\text{Me}_5\text{Li}$, $\text{C}_5\text{Me}_5\text{MgCl}(\text{THF})$, or $\text{C}_5\text{Me}_5\text{SnBu}_3$ failed.

In comparison to the cyclopentadienyl chromium species **11** and **12**, we note that complexes of the type $\text{MCp}(\text{O})_2\text{R}$ ($\text{M} = \text{Mo}, \text{W}$; $\text{Cp} = \text{C}_5\text{H}_5, \text{C}_5\text{Me}_5$; $\text{R} = \text{Me}, \text{CH}_2\text{SiMe}_3$) have been recently reported.³²⁻³⁴ Legzdins³⁴ reported that $\text{W}(\text{C}_5\text{Me}_5)(\text{O})_2\text{CH}_2\text{SiMe}_3$ could be cleanly converted to $\text{W}(\text{C}_5\text{Me}_5)(\text{O})(\text{Cl})_2\text{CH}_2\text{SiMe}_3$ on reaction with HCl , PCl_5 , or Me_3SiCl . We have been unable to prepare species of the type $\text{Cr}(\text{C}_5\text{H}_5)(\text{N}^t\text{Bu})\text{X}_3$ using analogous methodology. We suspect that a monoimido chromium(VI) species would be intrinsically less stable than its monooxotungsten congeners.

¹³C NMR Spectroscopy of (*tert*-Butylimido)chromium Complexes. The difference ($\Delta\delta$) in ¹³C NMR chemical shift between the quaternary carbon and the methyls of the *tert*-butylimido group ($\delta(\text{CMe}_3) - \delta(\text{CMe}_3)$) has been proposed^{9,35} to afford a qualitative indication of

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Table VI. ^{13}C NMR Chemical Shift Differences ($\Delta\delta$, ppm) in Cr(VI) *tert*-Butylimido Groups

X	$\Delta\delta$	
	Cr(N ^t Bu) ₂ X ₂	Cr(C ₅ H ₅)(N ^t Bu) ₂ X
Cl	52.7	
Br		49.2
CH ₂ SiMe ₃	40.7	42.9
CH ₂ CMe ₃	37.9	42.6
CH ₂ CMe ₂ Ph	39.9	42.8
OSiMe ₃	46.6 ^a	
10 ^b	38.4/39.8	
	37.6/40.6	

^aFrom ref 35. ^bCombinations of the two inequivalent imido groups in 10.

the degree of electron donation from the imido group to the metal center (Table VI). Thus it provides a convenient probe of electron distribution and Cr–N multiple bonding. The Δ values are additionally influenced by the nature of the other ligands bonded to chromium. In our series of complexes, which are all based on a Cr(N^tBu)₂ moiety, we have an opportunity to qualitatively assess the relative electron-donating ability of the other ancillary ligands. A more electron-donating ligand will tend to increase the nucleophilicity of the imido nitrogen atoms. The replacement of a chloride by a bromide appears to have little influence. We observe that the purely σ -donating alkyl groups gave rise to $\Delta\delta$ values of around 38–41 ppm, compared to values of around 51–52 ppm for the halide complexes Cr(N^tBu)₂X₂. These differences are indicative of considerable imido group π -donation to chromium in both cases but reduced for the compounds containing alkyl substituents. This implies that an alkyl group is a better electron donor to Cr(VI) than a chloride or bromide. The replacement of a halide by a formally 6-electron donor cyclopentadienyl anion would be expected to appreciably reduce the values of $\Delta\delta$ for the series Cr(C₅H₅)(N^tBu)₂X (vide infra) versus the series Cr(N^tBu)₂X₂. This is clearly not the case, although the trend for complexes within each series possessing identical ligands (X) is similar.

Related trends have been noted. Replacing an oxo ligand by a more electron releasing imido ligand in the series OsO₃(N^tBu), OsO₂(N^tBu)₂, and OsO(N^tBu)₃ causes $\Delta\delta$ to fall from 55 to 46 to 41 ppm, respectively.³⁵ Maatta has correlated ⁵¹V NMR chemical shifts of a series of V(N-tolyl)₃ complexes with the electronegativity and π -electron-donating ability of the ligand X,¹⁴ and ⁵¹V chemical shifts progressing to higher field as the σ -donating alkyl groups are replaced by ligands of increasing electronegativity and π -donating ability.^{14b}

Conclusion

This has afforded the first opportunity to comprehensively study the organometallic chemistry of Cr(VI). Simple routes to useful precursors on a synthetically useful scale have been developed. We have also synthesized a new class of stable high-valent chromium alkyl and metallacyclic species using a judicious choice of alkyl reagents, thus circumventing problems associated with reduction. The π -donating capability of two imido ligands has allowed the stabilization and isolation of chromium(VI) complexes; however, this also suppresses their reactivity.

Experimental Section

All experiments were performed in an argon atmosphere using Schlenk type glassware or in a Braun single-station drybox equipped with a –40 °C fridge under a nitrogen atmosphere. Elemental analyses were performed at Analytische Laboratorien,

Elbach, West Germany. Nuclear magnetic resonance spectra were recorded on Varian XL-200 or Varian VXR-300 spectrometers. Chemical shifts are reported in parts per million and referenced to the residual protons in deuterated solvents. Coupling constants are reported in hertz. Solvents were P.A. grade and were distilled from the appropriate drying reagent (sodium benzophenone ketyl for ether and THF, sodium for hexane and toluene) under argon prior to use. Deuterated solvents were dried over 4-Å molecular sieves.

Cr(N^tBu)₂(OSiMe₃)₂ (1). Compound 1 was prepared according to ref 8 on a larger scale and crystallized from hexane instead of hexamethyldisiloxane. CrO₂Cl₂ (9.5 mL, 18.0 g, 0.113 mol) in 20 mL of hexane was added dropwise over 5 min to a well-stirred solution of 84 mL (69.2 g, 0.48 mol) of *tert*-butyl(trimethylsilyl)amine in 200 mL of hexane at –20 °C. The mixture was allowed to warm to room temperature and subsequently refluxed for 1 h. The mixture was cooled to room temperature and filtered. The filtrate was concentrated to ca. 100 mL and stored at –30 °C to give 38 g, 87% yield after three crops, of Cr(N^tBu)₂(OSiMe₃)₂ as a very dark red (almost black) crystalline powder.

Cr(N^tBu)₂(py)Br₂ (2) and Cr(N^tBu)₂Br₂ (3). To a well-stirred solution of 15.2 g (41 mmol) of 1 and 7.4 g of pyridine in 200 mL of hexane was added 12.5 g (82 mmol) of Me₃SiBr at room temperature. The mixture was stirred overnight, during which an orange precipitate formed and the color of the mixture slowly changed to red. The orange precipitate was isolated by filtration and washed once with 20 mL of cold hexane to give 16.3 g (92% yield) of 2. Anal. Calcd for C₁₃H₂₃Br₂N₃Cr: C, 36.05; H, 5.35; Br, 36.89; N, 9.70; Cr, 12.00. Found: C, 35.86; H, 5.43; Br, 37.04; N, 9.60; Cr, 12.10. Compound 2 can be made pyridine-free by reaction with ethereal HBr at –78 °C and subsequent removal of pyridine-HBr by filtration, affording Cr(N^tBu)₂Br₂ (3) as a purple oil.

Cr(N^tBu)₂(py)Cl₂ (4) and Cr(O)(N^tBu)(OSiMe₃)₂ (6). To 11.0 g (30.0 mmol) of 1 dissolved in 180 mL of diethyl ether and cooled to –78 °C was added dropwise 60 mL of 1.0 M ethereal HCl over 5 min. After the addition was complete, the solution was allowed to warm to 25 °C. Removal of solvent, extraction with hexane, and filtration gave a mixture of Cr(N^tBu)₂Cl₂ (5) and Cr(O)(N^tBu)(OSiMe₃)₂ (6). Addition of 2.6 mL (32 mmol) of pyridine to this mixture of 5 and 6 in 60 mL of hexane gave a dark red solution, which was stirred overnight at 25 °C, whereupon 4 precipitated as an orange powder. This was filtered off and washed with 10 mL of hexane to give 5.0 g (14.9 mmol, 49% yield) of 4. Anal. Calcd for C₁₃H₂₃Cl₂N₃Cr: C, 45.36; H, 6.73; Cl, 20.60; N, 12.21; Cr, 15.10. Found: C, 45.15; H, 6.68; Cl, 20.38; N, 12.05; Cr, 14.95.

The red supernatant liquor from above was evaporated to give 5.2 g of a red oil, which was identified by NMR and elemental analysis as Cr(O)(N^tBu)(OSiMe₃)₂ (6): ¹H NMR (C₆D₆) δ 0.24 (s, 18 H), 1.42 (s, 9 H); ¹³C NMR (C₆D₆) δ 1.70 (OSiMe₃), 29.3 (NCMe₃), 84.3 (NCMe₃). Anal. Calcd for C₁₀H₂₇NCrO₃Si₂: C, 37.83; H, 8.57. Found: C, 38.14; H, 8.40.

Compound 6 can be prepared by the following alternative route: To a well-stirred solution of 0.43 g (1.15 mmol) of 1 in 30 mL of ether at –78 °C was added 25 μ L (1.4 mmol) of water and 1.4 mmol of ethereal HCl by syringe. The resulting red solution was stirred for 16 h at 25 °C. The normal workup procedure gave 6 in 89% yield.

Cr(O)(N^tBu)Cl₂. To 1.22 g (3.80 mmol) of Cr(O)(N^tBu)(OSiMe₃)₂ dissolved in 30 mL of toluene and cooled to –40 °C was added 0.834 g (4.0 mmol) of PCl₅ as a solid. This was stirred for 1 h at 25 °C, during which the color changed from dark red to purple. ³¹P NMR analysis of the reaction mixture showed conversion of PCl₅ to POCl₃ (δ = 2). The toluene was removed under vacuum, and the residual solid heated at 70 °C under vacuum to remove POCl₃, yielding Cr(O)(N^tBu)Cl₂ as a purple oil: ¹H NMR (C₆D₆) δ 1.17 (s, N^tBu). Anal. Calcd for C₄H₉Cl₂CrNO: C, 22.88; H, 4.32; Cl, 33.76; Cr, 24.76. Found: C, 24.44; H, 4.47; Cl, 33.93; Cr, 23.15.

General Workup Procedure for Preparation of Chromium Alkyl Compounds. The reaction mixture was evaporated to dryness and extracted with 25 mL of hexane. The extracts were filtered through a layer of diatomaceous earth and evaporated in vacuo to give the bisalkyl compounds as dark red oils.

Cr(N^tBu)₂(CH₂SiMe₃)₂ (7). To a suspension of 1.30 g (3.0 mmol) of **2** in 30 mL of diethyl ether at room temperature was added dropwise 6.0 mL (6.0 mmol) of a 1.0 M solution of Me₃SiCH₂MgCl in diethyl ether over 1 min. The dark red solution was stirred for 15 min. Standard workup gave **7** as a red oil. Anal. Calcd for C₁₆H₄₀CrSi₂N₂: C, 52.13; H, 10.94; N, 7.60; Si, 15.24; Cr, 14.10. Found: C, 50.03; H, 10.34; N, 7.53; Si, 14.55; Cr, 13.4. The low carbon analysis is indicative of residual MgClBr, which may be coordinated to chromium. Rapid filtration of a hexane solution of **7** through a thin layer of alumina served to remove a small (ca. 10%) quantity of MgClBr present in crude **7**, to give analytically pure **7**, albeit with some loss of yield. Found: C, 51.99; H, 10.76; Si, 15.05; Cr, 14.00.

On one occasion the monoalkyl product Cr(N^tBu)₂(CH₂SiMe₃)Br was observed, but we were unable to isolate it in a preparative reaction using 1 equiv of Me₃SiCH₂MgCl. Cr(N^tBu)₂(CH₂SiMe₃)Br: ¹H NMR (C₆D₆) δ 0.22 (s, 18 H, SiMe₃), 1.29 (s, 9 H, N^tBu), 2.75 (s, 2 H, CH₂).

Cr(N^tBu)₂(CH₂CMe₃)₂ (8). To a solution of 1.00 g (2.9 mmol) of **4** in 40 mL of toluene at -40 °C was added dropwise a solution of 0.59 g (2.9 mmol) of Zn(CH₂CMe₃)₂ in 5 mL of toluene. The resulting red-brown solution was allowed to reach room temperature and was stirred for 1 h. Standard workup gave **8**. Cr(N^tBu)₂(CH₂CMe₃)₂ could be obtained as a pure red oil by rapid filtration of the hexane solution through a thin layer of basic alumina in 67% yield (0.65 g). Anal. Calcd for C₁₈H₄₀CrN₂: C, 64.24; H, 11.98; N, 8.32; Cr, 15.45. Found: C, 64.00; H, 11.72; N, 8.42; Cr, 15.35.

Cr(N^tBu)₂(CH₂CMe₂Ph)₂ (9). A Grignard reaction between 0.5 g (20 mmol) of magnesium turnings and 2.7 g (15 mmol) of 1-chloro-2-methyl-2-phenylpropane was performed in diethyl ether, and the mixture filtered into a Schlenk flask. The concentration of the Grignard reagent was determined by titration as 0.82 M. This solution (3.5 mL) was added at -78 °C to a solution of 0.61 g (1.4 mmol) of **2** in 30 mL of toluene. The resulting brown solution was stirred for 1 h, during which time it was allowed to reach room temperature. Standard workup gave **9** as an analytically pure red-brown oil. Anal. Calcd for C₂₈H₄₄N₂Cr: C, 73.00; H, 9.63; Cr, 11.29. Found: C, 72.88; H, 9.70; Cr, 11.15.

Cr(N^tBu)₂[o-(CHSiMe₃)₂C₆H₄]₂ (10). To a well-stirred suspension of 1.50 g (3.5 mmol) of **2** in 40 mL of diethyl ether was added a suspension of 1.71 g (3.5 mmol) of o-C₆H₄[(CHSiMe₃)₂Li(TMEDA)]₂ in 20 mL of cold ether at -30 °C. The color changed immediately to purple, and the mixture was stirred for 4 h at room temperature. The solution was rapidly filtered through 4 cm of basic alumina to remove LiCl·TMEDA and the ether subsequently removed in vacuum. The oily residue was dissolved in 3 mL of hexane and stored overnight at -30 °C to give 0.98 g (64% yield) of **10** as very dark red crystals. Anal. Calcd for C₂₂H₄₂N₂Si₂Cr: C, 59.68; H, 9.56; N, 6.33; Si, 12.69; Cr, 11.74. Found: C, 59.70; H, 9.14; N, 6.25; Si, 12.75; Cr, 11.70.

Mg(C₅H₅)₂(THF)_{2.5}. To a solution of 3.0 g (35 mmol) of diethylmagnesium in 50 mL of THF was added 7 mL (125 mmol) of freshly distilled cyclopentadiene, and the mixture stirred overnight at 50 °C. The solvent was removed in vacuo, and the residue became solid on trituration with hexane. The white powder was isolated by filtration and washed twice with hexane to give 7.7 g of Mg(C₅H₅)₂(THF)_{2.5}: ¹H NMR (C₆D₆) δ 6.16 (s, 10 H, C₅H₅), 3.29 (m, 10 H, THF), 1.25 (m, 10 H, THF).

Cr(C₅H₅)(N^tBu)₂Br (11). To a suspension of 1.85 g (4.3 mmol) of **2** in 50 mL of diethyl ether at -78 °C was added dropwise over 2 min 0.70 g (2.1 mmol) of Mg(C₅H₅)₂(THF)_{2.5} in 10 mL of THF. The solution was allowed to warm to 25 °C and stirred for an additional 2 h. The solvent was removed in vacuo, and the residual dark solid extracted with hexane and filtered to afford Cr(C₅H₅)(N^tBu)₂Br as a dark brown-black microcrystalline solid, which can be crystallized from hexane at -40 °C. Anal. Calcd for C₁₃H₂₃CrBrN₂: C, 46.03; H, 6.83; Cr, 15.33, Br, 23.55. Found: C, 45.89; H, 6.69; Cr, 15.45; Br, 23.27. Compound **11** is unstable in solution (40% decomposition after 16 h in C₆D₆ at 25 °C) and decomposes to an unidentified product.

Cr(C₅H₅)(N^tBu)₂Cl (12). To a suspension of 1.78 g (5.2 mmol) of **4** in 50 mL of diethyl ether at -78 °C was added dropwise over 2 min 0.87 g (2.6 mmol) of Mg(C₅H₅)₂(THF)_{2.5} in 10 mL of THF. Workup gave a green hexane solution, which was crystallized at

-40 °C to give 0.5 g (1.7 mmol) of Cr(C₅H₅)(N^tBu)₂Cl as purple crystals, yield 33%. The compound is unstable in C₆D₆ and decomposes to an unidentified product (16 h, 25 °C). Anal. Calcd for C₁₃H₂₃CrClN₂: C, 52.97; H, 7.86; Cr, 17.64, Cl, 12.03. Found: C, 51.16; H, 7.92; Cr, 18.6; Cl, 12.42.

Cr(C₅H₅)(N^tBu)₂Me (13). To a solution of 0.34 g (0.8 mmol) of Cr(C₅H₅)(N^tBu)₂Br in 25 mL of diethyl ether at -78 °C was added dropwise a solution of 57 mg (0.4 mmol) of MgMe₂·dioxane in 10 mL of THF. The solution became red, and the mixture was stirred for 1 h, during which it warmed to room temperature. Standard workup gave a red oil. This was dissolved in 2 mL of hexane and stored overnight at -40 °C, during which time a small quantity of solid deposited. The mother liquor was carefully removed from the unwanted solid by pipet and evaporated in vacuo to give **13**. The same procedure was used to prepare Cr(C₅H₅)(N^tBu)₂CH₂CMe₃ (**14**), Cr(C₅H₅)(N^tBu)₂CH₂SiMe₃ (**15**), and Cr(C₅H₅)(N^tBu)₂CH₂CMe₂Ph (**16**).

One-Pot Procedure for Cr(C₅H₅)(N^tBu)₂CH₂CMe₃ (14). To circumvent the problems associated with an unstable starting material, a one-pot procedure starting from Cr(N^tBu)₂(py)Br₂ (**2**) was developed.

To a solution of 2.72 g (6.3 mmol) of **2** in 100 mL of diethyl ether cooled to -78 °C was added dropwise a solution of 1.0 g (3.1 mmol) of Mg(C₅H₅)₂(THF)_{2.5} in 20 mL of THF. The mixture was stirred for 1 h, during which it was allowed to warm to room temperature. The mixture was then recooled to -78 °C, and a solution of 0.63 g (3.1 mmol) of Zn(CH₂CMe₃)₂ in 10 mL of toluene added dropwise. The dark red suspension was stirred for an additional hour at room temperature. The standard workup procedure gave 1.75 g (83% overall isolated yield) of **14** as an impure dark red oil. Anal. Calcd for C₁₈H₃₄CrN₂: C, 65.42; H, 10.37; Cr, 15.73; N, 8.48, Br, 0.0. Found: C, 62.49; H, 9.66; Cr, 15.10; N, 8.04; Br, 4.63. The bromide analysis is indicative of the presence of either ZnBr₂ or MgClBr. Filtration of a hexane solution through a thin layer of alumina afforded **14**. Found: C, 63.37; H, 10.01; Cr, 16.55; N, 8.22.

[Cr(C₅H₅)(N^tBu)(μ-N^tBu)]₂ (17). To a solution of 0.1 g (0.295 mmol) of **11** in 25 mL of ether at -78 °C was added 0.3 mL of 1 M LiEt₃BH by syringe. The color changed to orange on warming to 25 °C. After 0.5 h the solvent was removed, and the residue extracted with pentane and filtered to afford solid **17**: ¹H NMR (C₆D₆) δ 1.06 (CMe₃), 1.63 (CMe₃), 5.76 (C₅H₅); ¹³C NMR (C₆D₆) δ 31.1 (CMe₃), 34.9 (CMe₃), 72.1 (CMe₃), 74.9 (CMe₃), 108.1 (C₅H₅).

[Cr(Me₂PCH₂CH₂PMe₂)(N^tBu)₂Br] (18). To 1.03 g (2.37 mmol) of **2** dissolved in 30 mL of toluene and cooled to -30 °C was added 0.36 g of Me₂PCH₂CH₂PMe₂ (1 equiv) in 3 mL of toluene. The orange solution changed immediately to a yellow flocculent suspension. This was filtered off and washed with 3 × 10 mL of pentane to give a bright yellow powder, which was crystallized from CH₂Cl₂/pentane, yield 1.06 g (89%). Because **18** is insoluble in hexane, ether, and toluene but quite soluble in dichloromethane, we assume it to be cationic; ¹H NMR (CD₂Cl₂) δ 1.54 (s, 18 H, CMe₃), 1.95 (d, 6 H, ²J_{PH} = 11.1 Hz, PMe₂), 2.14 (d, 6 H, ²J_{PH} = 12.1 Hz, PMe₂), 2.62 (br m, 2 H, CH₂PMe₂), 3.05 (br m, 2 H, CH₂PMe₂); ¹³C NMR (CD₂Cl₂) δ 15.57 (d, ¹J_{CP} = 27 Hz, PMe₂), 18.19 (d, ¹J_{CP} = 29.4 Hz, PMe₂), 23.95 (d, ¹J_{CP} = 23 Hz, PCH₂), 30.27 (s, CMe₃), 79.7 (s, CMe₃), the other CH₂ resonance was obscured by CMe₃; ³¹P NMR (CD₂Cl₂) δ 33.52 (d, J_{PP} = 58.7 Hz), 57.75 (d, J_{PP} = 58.7 Hz).

X-ray Structure Analysis for 10. A single crystal of **10** was mounted under nitrogen in a thin-walled glass capillary under nitrogen and held in place with silicone grease. All diffraction experiments were carried out at 295 K on a Nicolet P3m four-circle diffractometer using graphite monochromated Mo K α X-radiation, $\lambda = 0.71069$ Å. Unit-cell dimensions were determined from 15 centered reflections in the range 27.0° < 2 θ < 28.0°. Details of crystal data collection and reduction are given in Table IV. A total of 4229 diffracted intensities, including check reflections, were measured in a unique quadrant of reciprocal space for 4.0° < 2 θ < 50.0° by Wyckoff ω scans; for 2 θ > 40.0° only those reflections with count rates >20 counts s⁻¹ were recorded. Three check reflections remeasured after every 100 ordinary data showed a variation of $\pm 2\%$ over the period of data collection, and hence an appropriate correction was applied. The absorption correction was based on 240 azimuthal scan data, maximum and minimum transmission coefficients being 0.900 and 0.798, respectively.

Lorentz and polarization corrections were applied. Structure solution was by conventional heavy-atom (Patterson and difference Fourier) methods and refinement by blocked cascade full-matrix least-squares (with weights w set equal to $[\sigma_c^2(F_o) + gF_o^2]^{-1}$, where $\sigma_c^2(F_o)$ is the variance in F_o due to counting statistics). All non-hydrogen atoms were assigned anisotropic displacement parameters, and all hydrogen atoms fixed isotropic displacement parameters. All non-hydrogen atoms were refined without positional constraints. All hydrogen atoms were constrained to idealized geometries (C-H 0.96 Å, H-C-H 109.5°) except for H(1) and H(2), which were refined without positional constraints. Residuals of convergence are listed in Table IV. All calculations were carried out with Nicolet proprietary software using complex

scattering factors taken from ref 36.

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Supplementary Material Available: Tables of hydrogen atom parameters and anisotropic thermal parameters (4 pages); tables of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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Multiple Bonds between Transition Metals and Main-Group Elements. 74.¹ Five-Membered Rhenacycles through Condensation Reactions of Methyltrioxorhenium(VII) with Bidentate Ligands. X-ray Crystal Structures of 8-Oxyquinolino and Catecholato Complexes

Janos Takacs,[†] Paul Kiprof, Jürgen Riede, and Wolfgang A. Herrmann*

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-8046 Garching bei München, West Germany

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Methyltrioxorhenium(VII), CH_3ReO_3 (1), undergoes condensation reactions with aromatic bidentate ligands of type $\text{HO}\cdots\text{X}$ ($\text{X} = \text{N}, \text{NH}_2, \text{OH}$) to yield products with strongly ligand-dependent structures. Mild conditions are characteristic of these condensation reactions. Thus, reactions of 1 with catechols 1,2-(HO)₂ $\text{C}_6\text{H}_2\text{RR}'$ -3,4 in the presence of pyridine give compounds **2a-c** of general formula $\text{CH}_3\text{Re}(\text{O})_2(1,2\text{-O}_2\text{C}_6\text{H}_2\text{RR}'\text{-3,4})(\text{NC}_5\text{H}_5)$ in high yields. The single-crystal X-ray diffraction study of the parent catecholato derivative **2a** ($\text{R} = \text{R}' = \text{H}$) reveals an octahedral ligand sphere around the rhenium atom, with cis oxo ligands and the pyridine in trans position with respect to the methyl group. Treatment of **2a** with anhydrous hydrogen chloride yields the ionic complex **3a** of formula $[\text{C}_5\text{H}_5\text{NH}]^+[\text{CH}_3\text{Re}(\text{O})_2(1,2\text{-O}_2\text{C}_6\text{H}_4)\text{Cl}]^-$, resulting from nucleophilic replacement of the pyridine ligand by a chloride ion. Reaction of 1 with the heterobifunctional ligand 2-aminophenol yields the bis-substituted amidophenolato derivative $\text{CH}_3\text{Re}(\text{O})[1,2\text{-O}(\text{HN})\text{C}_6\text{H}_4]_2$ (**4**). While the bis(thiophenolato) analogue of **4** could not be isolated, the pyridine adduct of the mono(amidothiophenolato) derivative $\text{CH}_3\text{Re}(\text{O})_2[1,2\text{-S}(\text{HN})\text{C}_6\text{H}_4](\text{C}_5\text{H}_5\text{N})$ (**5**) is easily obtainable. Smooth reaction of 1 with 1 equiv of the chelating ligand 8-hydroxyquinoline results in the formation of the binuclear compound $(\mu\text{-O})[\text{CH}_3\text{Re}(\text{O})_2(8\text{-oxyquinolino})]_2$ (**6**) in 90% yield. According to a single-crystal X-ray study, the centrosymmetric molecule consists of two corner-sharing distorted octahedra with a (linear) bridging oxo ligand. Most of the novel oxorhenium(VII) condensation products hydrolyze to the respective precursor compounds. The *aliphatic* analogues of this type of condensation products could not be isolated.

Introduction

High oxidation state organometallic chemistry has rapidly gained impetus in recent years. The general interest in this field stems partly from the potential of such complexes to promote facile transformations of organic compounds in a number of chemical processes. Many catalytic reactions such as olefin metathesis, polymerization, etc., have been known to involve high-valent organometallic species, and evidence is mounting that such intermediates are also important in other types of reactions such as metal oxide catalyzed olefin oxidation, hydroxylation, etc.^{2,3} Biological systems featuring active sites with transition metals in medium-to-high oxidation states (Fe, Mo, etc.) also provide stimulus for work in this area.⁴ At present,

rhenium derives its importance mainly from the former field. However, a very promising new area related to bioinorganic chemistry is the synthesis of radiopharmaceuticals, based on the easily accessible isotopes ¹⁸⁶Re and

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[†] Presently Alexander von Humboldt Fellow on leave from the Research Group for Petrochemistry of the Hungarian Academy of Sciences, Veszprem/Hungary.