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Synthesis and Characterization of an Organochromium Compound Bearing Three Sterically Demanding Alkenyl Ligands

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Summary: The synthesis and characterization of tris(alkenyl)chromium compounds has been facilitated by the use of a sterically demanding alkenyl ligand, the ligand being derived from the Wittig coupling of 2-adamantanone with a benzylidenephosphorane.

Introduction

While homoleptic alkenyl compounds were first reported in 1977,[1] very little work has since been reported concerning this class of compounds. Our interest in the synthesis and reactivity of three-coordinate complexes[2] now leads us to explore the use of alkenyl ligands in the context of chromium chemistry. An attractive feature of the alkenyl fragment as a ligand (ancillary or otherwise) is that the metal−alkenyl M−C bond is expected to be strong relative to certain other M−C bond types.

Herein we report the design and synthesis of a sterically demanding alkenyl ligand and its initial implementation in chromium chemistry. The alkenyl fragment in question is −C(Ad)Ar (Ad = 2-adamantylidene, Ar = 3,5-$C_6H_3Me_2$). The steric bulk provided by the chosen substituents is intended to inhibit dimerization and disproportionation reactions for complexes containing three −C(Ad)Ar ligands.

Known alkenyl−chromium compounds are based on the 2,2-dimethyl-1-phenylethenyl ligand,[1,3] essentially a smaller variant of the new ligand we report here. However, it was found that the incompletely characterized chromium compound CrL_3(THF) (where L = −C[CMe_2]Ph) was thermally unstable and disproportionated to the crystallographically characterized CrL_4. Hydrocarbyl ligands have in general not been extensively utilized as supporting ligands for three-coordinate complexes, mesityl and $CH(SiMe_3)_2$ being the most commonly utilized C-donor ligands.[2] Three-coordinate hydrocarbyl compounds of chromium include $Cr(CH[SiMe_3]_2)_3$[4,5] and $Cr(4\text{-cam})_3$ (4-cam = 2,2,3-trimethylbicyclo[2.2.1]hept-1-yl).[6] There are also some four-coordinate Lewis base adducts of tris(hydrocarbyl) chromium species including $Cr(THF)(Mes)_3$ (Mes = 2,4,6-$C_6H_2Me_3$)[7] and $Cr(THF)(C[CMe_2]Ph)_3$. Of these compounds, $Cr(CH[SiMe_3]_2)_3$ is the only one that has been crystallographically characterized.[5]

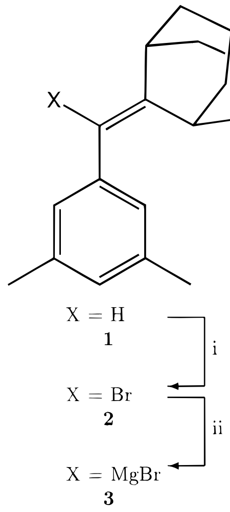

Figure 1. Olefin 1 was obtained by Wittig methodology (52.5%). (i) Treatment of **1** with bromine followed by KO^tBu gives vinyl bromide **2** (78%). (ii) Vinyl Grignard reagent **3** is obtained in 91% yield upon treatment of **2** with Mg in THF.

Results and Discussion

The ligand synthesis is depicted in Figure 1. The phosphonium salt from α-bromomesitylene and PPh_3 was deprotonated in situ, generating the desired phosphorane, which was then treated with 2-adamantanone under Wittig conditions to provide olefin **1**.[8] Olefin **1**

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[1] Cardin, C. J.; Cardin, D. J.; Kelly, J. M.; Norton, R. J.; Roy, A. *J. Organomet. Chem.* **1977**, *132*, C23.

[2] (a) Cummins, C. C. *Prog. Inorg. Chem.* **1998**, *47*, 685. (b) Cummins, C. C. *J. Chem. Soc., Chem. Commun.* **1998**, 1777.

[3] Cardin, C. J.; Cardin, D. J.; Kelly, J. M.; Norton, R. J.; Roy, A.; Hathaway, B. J.; King, T. J. *J. Chem. Soc., Dalton Trans.* **1983**, 671.

[4] Barker, G. K.; Lappert, M. F. *J. Organomet. Chem.* **1974**, *76*, C45.

[5] Barker, G. K.; Lappert, M. F.; Howard, J. A. K. *J. Chem. Soc., Dalton Trans.* **1978**, 734.

[6] Bower, B. K.; Tenant, H. G. *J. Am. Chem. Soc.* **1972**, *94*, 2512.

[7] Stolze, G. *J. Organomet. Chem.* **1966**, *6*, 383.

[8] Synthesis of **1**: α-bromomesitylene (124.9 g, 0.627 mol, 1 equiv) and PPh_3 (164.5 g, 0.627 mol, 1 equiv) were weighed into a flask and slurried in toluene (1 L). The mixture was refluxed overnight, cooled, and filtered. The resulting crude phosphonium salt was washed with toluene (300 mL) and petroleum ether (300 mL) and obtained as a white powder (258.86 g, 89%). The phosphonium salt (176 g, 0.38 mol) was dissolved in dry THF (650 mL) in the glovebox. Lithium diisopropylamide (200 mL, 2.0 M in THF/heptane/ethylbenzene, 0.40 mol) was added, and the reaction mixture was stirred for 10 min. 2-Adamantanone (57.3 g, 0.38 mol) was added, and the slurry was refluxed 18 h under. The reaction mixture was cooled, concentrated, and extracted with diethyl ether (4 × 400 mL). The combined extracts were concentrated, and the light-yellow solid **1** was recrystalized from boiling methanol. Two crops of crystals were collected and dried *in vacuo* (48.32 g, 52.5%). ^1H NMR (C_6D_6, 300 MHz): δ 1.6-2.0 (m, 12H, adamantyl), 2.18 (s, 6H, aryl methyl), 2.50 (s, 1H, adamantyl), 3.36 (s, 1H, adamantyl), 6.337(s, 1H, vinyl), 6.741 (s, 1H, aryl para), 6.989 (s, 2H, aryl ortho).

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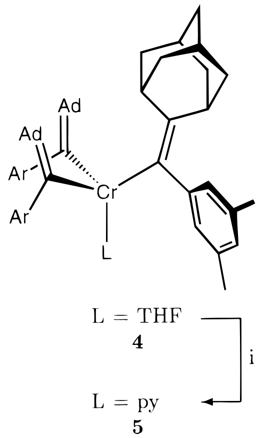

Figure 2. Treatment of $CrCl_3$ with **3** gave **4** in 68% yield (Ar = 3,5-$C_6H_3Me_2$, Ad = 2-adamantylidene). (i) Compound **4** was found to react with pyridine to give **5** as blue needles (81% yield). Other Lewis bases (triethylphosphine, tetrahydrothiophene) failed to react with **4**.

was sequentially brominated and dehydrohalogenated to give the corresponding bromoolefin **2**,[9] which in turn was converted to the Grignard reagent **3** upon refluxing with magnesium turnings in THF. Grignard **3** was isolated as a white powder consisting of a presumed mixture of $Mg(C[Ad]Ar)_2(THF)_x$ and $Mg(C[Ad]Ar)(Br)(THF)_x$.[10]

The chromium trisalkenyl compound $Cr(THF)(C[Ad]Ar)_3$ (**4**) was prepared by reaction of the Grignard reagent **3** with anhydrous $CrCl_3$ in diethyl ether (Figure 2). Addition of dioxane and filtration of the mixture, followed by partial removal of volatile components, provided **4** in 68% yield as blue crystals.[11] The compound is paramagnetic and exhibits a solid-state magnetic moment of 3.67 μ_B, as measured by SQuID magnetometry, indicative of a high spin d^3 system. The visible spectrum in C_6H_6 consists of a single broad band at λ 590 nm (ϵ 1300 M^{-1} cm^{-1}).

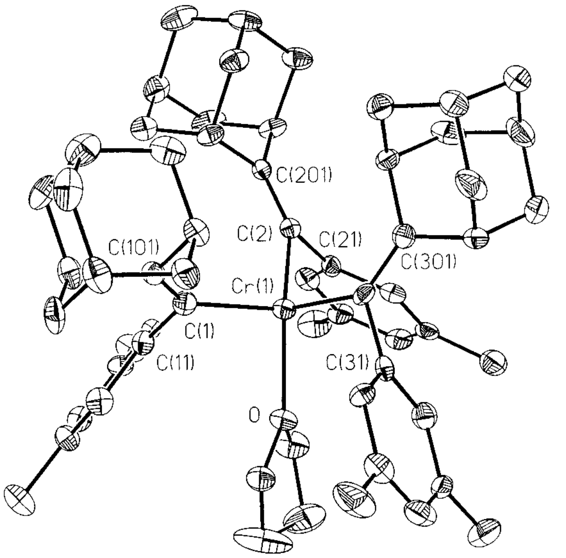

Figure 3. Drawing of $Cr(THF)(C[Ad]Ar)_3$ (**4**) (35% probability ellipsoids). Selected distances (Å) and angles (deg): Cr(1)−O, 2.174(4); Cr(1)−C(1), 2.039(7); Cr(1)−C(2), 2.048(6); Cr(1)−C(3), 2.055(7); C(1)−Cr(1)−C(2), 104.7(3); C(1)−Cr(1)−C(3), 112.3(3); C(2)−Cr(1)−C(3), 106.0(3); C(1)−Cr(1)−O, 97.3(2); C(2)−Cr(1)−O, 130.4(2); C(3)−Cr(1)−O, 105.6(2).

The solid-state structure of $Cr(THF)(C[Ad]Ar)_3$ is shown in Figure 3.[12] The THF is located in a pocket comprised of the three aryl rings. The Cr−C bond lengths are 2.039(7), 2.048(6), and 2.055(7) Å. These distances compare well with the value of 2.07(1) Å found for $Cr(CH[SiMe_3]_2)_3$.[5] In comparing the Cr−C bond lengths to those found in other chromium alkenyl compouds, the bond lengths are similar to those in $Cr(C[CMe_2]Ph)_4$ (2.049(12), 2.027(13), 2.032(13), and 2.033(11) Å)[3] and shorter than the length found in the much more electron-rich $Cr(CMe{=}CMeCH_2CH{=}CH_2)(C_3H_5)(PMe_3)_2$ (2.113(5) Å).[13] The C=C bond lengths are unexceptional and are 1.347(9), 1.323(8), and 1.349(9) Å. The issue of donation of π electron density from the double bond into empty metal orbitals, or conversely π-backbonding, has previously been investigated by comparison of the solid-state structures of $Cr(C[CMe_2]Ph)_4$ and $Sn(C[CMe_2]Ph)_4$. It was concluded that there is a real, but statistically insignificant, lengthening of the C=C double bonds in the chromium structure as compared to the tin structure.[3]

To address the question of Cr−C π-bonding in **4**, we performed density functional theory (DFT) calculations[14] on the hypothetical molecule $Cr(OMe_2)(vinyl)_3$ (**7**) using the core bond angles found in the X-ray structure for **4**. These calculations, the results of which are summarized in Table 1 (see also Figure 4), reveal

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[9] Synthesis of **2**: olefin **1** (58.4 g, 0.23 mol) was dissolved in CH_2Cl_2 (500 mL). Br_2 (13 mL, 40.7 g, 0.25 mol, 1.1 equiv) was dissolved in CH_2Cl_2 to give a total volume of 100 mL. The bromine solution was SLOWLY added to the stirring solution of **1**. The reaction mixture was stirred for 1.5 h, concentrated, and brought into the glovebox. Dry THF (500 mL) was added, and the solution was chilled. To the chilled solution was added KO^tBu (32 g, 0.29 mol, 1.25 equiv), the flask was closed, and the mixture was allowed to stir overnight under N_2. The reaction mixture was concentrated and added to a mixture of water (400 mL) and diethyl ether (400 mL). The organic layer was then washed with water (200 mL), and the combined aqueous layers were washed with ether (100 mL). The combined organic extracts were dried with $MgSO_4$ and concentrated. The crude solid **2** was then recrystallized from boiling methanol (2 L). The crystalline product was then dried in vacuo overnight (59.6 g, 78%). ^1H NMR (C_6D_6, 300 MHz): δ 1.5−1.9 (m, 12H, adamantyl H), 2.07 (s, 6H, aryl methyl), 2.85 (s, 1H, adamantyl), 3.55 (s, 1H, adamantyl), 6.68 (s, 1H, aryl), 7.07 (s, 2H, aryl).

[10] Synthesis of **3**: bromide **2** (38.05 g, 0.114 mol) was dissolved in dry THF (200 mL), and 10 mL of the solution was cannula-transferred onto Mg turnings (6 g, 0.25 mol). The reaction mixture was heated until initiation began, at which point the cannula transfer was completed. The reaction mixture was refluxed for 1 h, cooled, and brought into the glovebox. It was filtered through a Büchner funnel with additional THF (100 mL) and concentrated to yield a yellow oil. The oil was slurried in pentane (100 mL) to give a white solid, which was collected on a filter frit (52.05 g, 91%) One-pulse ^1H NMR indicated the product to be a mixture of $Mg(C[Ad]Ar)(Br)(THF)_x$ (δ 2.25 for aryl methyl H) and $Mg(C[Ad]Ar)_2(THF)_x$ (δ 2.31 for aryl methyl H).

[11] Synthesis of **4**: Grignard **3** (12.9 g, 0.026 mol, 3.0 equiv) and anhydrous $CrCl_3$ (1.7 g, 0.011 mol, 1.25 equiv) were slurried in diethyl ether (500 mL). The suspension was allowed to stir for 48 h. Dioxane (10 mL) was added, the reaction mixture was allowed to stir for an additional 2 h, and then the solid was allowed to settle. The mixture was filtered through Celite, washed with diethyl ether (40 mL), and concentrated to 100 mL. After standing for 2 h the mixture was once again filtered to collect **4** as blue crytals (5.1 g, 68%). Anal. Calcd for $C_{61}H_{77}CrO$: C, 83.42; H, 8.84. Found: C, 83.33 H, 8.99. μ_{eff} (SQuID) = 3.67 μ_B.

[12] Crystal Data. **4**: $C_{61}H_{77}CrO$, M_w = 878.23, triclinic $P\bar{1}$, a = 11.3534(10) Å, b = 11.6451(10) Å, c 20.165(2) Å, α = 76.556(2)°, β = 77.9370°, γ = 73.5660(10)°, V = 2457.5(4) Å^3, Z = 2, D_{calc} = 1.187 Mg/m^3, absorption coefficient 0.274 mm^{-1}, $F(000)$ = 950, number of reflections collected = 7262, number of independent reflections = 4531, GOF = 1.234, R = 0.0762, wR_2 = 0.1372.

[13] Betz, P.; Jolly, P. W.; Kruger, C.; Zakrzewski, U. *Organometallics* **1991**, *10*, 3520.

Table 1. Results of DFT Calculations on Hypothetical 7[14] [a]

atom	charge	bond	op	length (Å)
		$Cr(OMe_2)(vinyl)_3$		
Cr	+0.4827	Cr−O	0.0868	2.201
O	−0.0946	Cr−C	0.2281	1.922
C_α	−0.1952	C═C	0.4935	1.353
C_β	−0.1113	C−O	0.2090	1.467
C_{methyl}	−0.0226			
		Ethylene		
C	−0.0908	C═C	0.5923	1.334
		Ethane		
C	−0.1130	C−C	0.3516	1.532
		$CrMe_3$		
Cr	+0.5972	Cr−C	0.2956	1.989

[a] Constraints used for geometry optimization: quartet state, all Cr−C bond lengths equal, all C═C bond lengths equal, all core bond angles same as found by X-ray for **4**. Average overlap populations (op's) or Hirschfield charges are provided where relevant. Results of similar calculations on ethylene, ethane, and planar trimethylchromium are included for comparison.

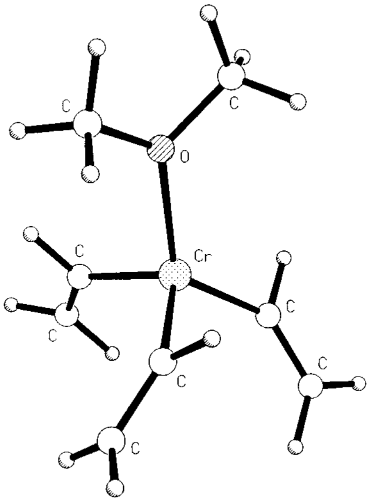

Figure 4. Calculated structure of $Cr(OMe_2)(vinyl)_3$ (**7**) with the same core geometry as **4**. See also Table 1.

that the the C═C overlap population is reduced from that found in ethylene, consistent with partial transfer of electron density from Cr into the C═C π^* orbital. It must be noted, however, that the calculated structure of **7** represents only an approximation to the full structure of **4**, such that any electronic consequences of steric effects are lost within the context of this analysis.

Inasmuch as some three-coordinate chromium(III) complexes do not display pronounced Lewis acidity, a noteworthy feature of the structure of **4** is the presence of the bound THF molecule. The Cr−O bond length of 2.174(4) Å is similar to the Cr−O bond length of 2.225(10) Å found for $Cr(Ph)_3(THF)_3$[15] and is longer than the Cr−O bond lengths in $CrCl_3(THF)_3$.[16] Siloxide[17] and amide[18] ancillary ligands have led to THF-free three-coordinate chromium(III) derivatives, even when prepared with THF as the reaction solvent. Chromium(III) derivatives of non-π-donor ligands such as $Cr(THF)(Mes)_3$ and $Cr(THF)(C[CMe_2]Ph)_3$ have, in contrast, only been described as THF adducts. An exception is $Cr(CH[SiMe_3]_2)_3$, which was reported not to react with pyridine.

Pyridine addition to a pentane solution of $Cr(THF)(C[Ad]Ar)_3$ resulted in rapid precipitation of $Cr(py)(C[Ad]Ar)_3$ (**5**) as dark blue needles (Figure 2).[19] Pyridine adduct **5** exhibits physical properties similar to those for THF adduct **4**, with a magnetic moment of 3.83 μ_B and a single band in the visible spectrum (λ 585 nm, ϵ 1600 M^{-1} cm^{-1}, C_6H_6). The THF ligand was not displaced by an excess of PEt_3, *N*,*N'*-tetramethylethylenediamine (TMEDA), or tetrahydrothiophene.

The Lewis acidity exhibited by the $Cr(C[Ad]Ar)_3$ fragment (**6**) can be attributed to the lack of π-donation by the ligands, resulting in a highly electron-deficient Cr center. Chromium trisamide compounds have (in C_{3v} symmetry) a formal electron count of 13e, with two of the available nitrogen lone-pair orbitals having the proper symmetry for interaction with low-lying empty metal orbitals. In contrast, the fragment **6** has a formal electron count of 9e. Even so, the reactivity of **4** with Lewis bases evidently can be attenuated by steric factors: THF and pyridine are able to fit into the "pocket" comprised of the Ar substituents, while TMEDA and PEt_3 do not displace THF.

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Supporting Information Available: Full synthesis and characterization data for all new compounds, details of the DFT calculations, and tables of SQuID data for **4** and **5**; tables of atomic coordinates, thermal parameters, and bond distances and angles for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) *ADF 2.3.0*; Theoretical Chemistry, Vrije Universiteit: Amsterdam. (a) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41. (b) te Velde, G.; Baerends, E. J. *J. Comput. Phys.* **1992**, *99*, 84. (c) Fonseca-Guerra, C.; Visser, O.; Snijders, J. G.; te Velde, G.; Baerends, E. J. *Methods and Techniques in Computational Chemistry: METECC-95*; 1995; 305.

(15) Khan, S. I.; Bau, R. *Organometallics* **1983**, *2*, 1896.

(16) Cotton, F. A.; Duraj, S. A.; Powell, G. L.; Roth, W. J. *Inorg. Chim. Acta* **1986**, *113*, 81.

(17) Blanchard, H.; Hursthouse, M. B.; Sullivan, A. C. *J. Organomet. Chem.* **1988**, *341*, 367.

(18) Alyea, E. C.; Basi, J. S.; Bradley, D. C.; Chisholm. M. H. *J. Chem. Soc., Chem. Commun.* **1968**, 495.

(19) Synthesis of **5**: THF adduct **4** (183.3 mg, 0.209 mmol, 1 equiv) was dissolved in pentane (15 mL). Pyridine (104 mg, 1.31 mmol, 6.3 equiv) in pentane (2 mL) was added dropwise, and the reaction mixture was allowed to stand for 2 h. The mixture was filtered to collect 150 mg (81%) of analytically pure needles. Anal. Cacld for $C_{57}H_{69}CrN$: C, 84.12; H, 8.43; N, 1.58. Found: C, 83.81; H, 8.30; N, 1.30. μ_{eff}(SQuID) = 3.83 μ_B.