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Organometallic Chemistry of the Transition Elements. 5. An Improved Synthetic Route to (Arene)chromium π-Complexes[1]

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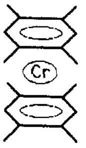
A new, solvent-free synthetic route to bis(η^6-arene)chromium(0) compounds incorporating ligands with low vapor pressures is discussed. The direct reaction of chromium metal atoms with both model ligands (durene, pentamethylbenzene, and hexamethylbenzene) and ligands containing two sites at which π-complexation to metal atoms can occur (biphenyl, diphenylmethane, and *trans*-stilbene) is described. The preparation and characterization of several of the resulting compounds are reported for the first time via the direct metal atom synthesis technique.

Introduction

Since Timms reported the first direct metal atom synthesis of a bis(η^6-arene)chromium(0) compound—bis(η^6-benzene)chromium(0)—most arenes possessing high vapor pressure have been extensively studied.[2] Bis(η^6-arene)chromium(0) compounds in which the free arenes do not exhibit a high vapor pressure have been relatively inaccessible by this method. In attempts to utilize the conventional static reactor with low vapor pressure arenes for the production of bis(η^6-arene)chromium(0) compounds, heated ligand inlet systems, have been employed. Such modifications are generally inefficient because the deposition rate of the ligand is difficult to control.

Timms[3] and Ozin[4] have reported the design of different reactors—rotating reactors—that should more efficiently deal with nonvolatile ligands. In these approaches, metal is evaporated into a solution consisting of the ligand in a low vapor pressure, inert solvent. Product isolation from either the excess ligand or the solvent is often both difficult and time consuming.

We have discovered that bis(η^6-arene)chromium(0) compounds can be synthesized by reacting chromium atoms directly with solid substrates at 77 K in the absence of any solvent. We report here the synthesis of three model compounds using this straightforward approach, viz., bis(η^6-durene)chromium(0) (I), bis(η^6-pentamethylbenzene)chromium(0) (II), and bis(η^6-hexamethylbenzene)chromium(0) (III). These model compounds I, II, and III were prepared by both the conventional method[5] and our solvent-free route in order to prove the feasibility of our new synthetic technique.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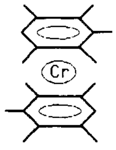
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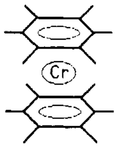
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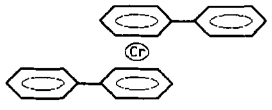
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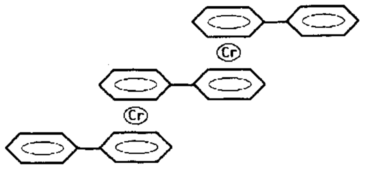
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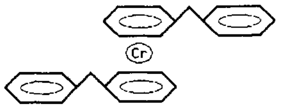
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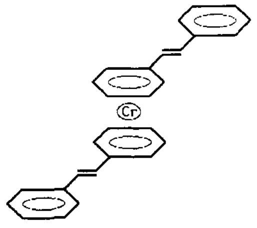
VII

Our main interests lie in the synthesis of polynuclear π-complexes of chromium. Accordingly, we have prepared and characterized bis(η^6-biphenyl)chromium(0) (IV), (μ-η^6:η^6-biphenyl)bis[(η^6-biphenyl)chromium(0)] (V), bis(η^6-diphenylmethane)chromium(0) (VI), and bis(η^6-*trans*-stilbene)chromium(0) (VII) using the technique reported here. These compounds are all potential precursors to polynuclear species since they each contain additional aromatic sites at which coordination to a metal atom could

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[1] Part 4: L. H. Simons and J. J. Lagowski, *J. Organomet. Chem.*, **249**, 195 (1983).

[2] P. L. Timms, *J. Chem. Soc. D*, 1033 (1969).

[3] R. Mackenzie and P. L. Timms, *J. Chem. Soc., Chem. Commun.* 650 (1974).

[4] M. Moskovits and G. A. Ozin, "Cryochemistry", Wiley-Interscience, New York, 1976, p 129.

[5] I, II, and III were synthesized by using a conventional static reactor with respective yields of 6.83%, 3.17%, and <1%.

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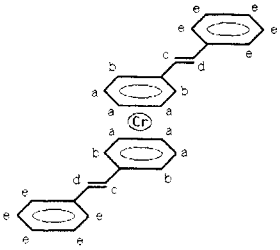
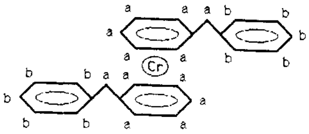
Table I. Characteristics of VI and VII

		^{1}H NMR^a			yields,^{b}	anal.^{c}		physical
compd	struct	assn.	mult	shift	%	m/e(calcd)	m/e(measd)	characteristics
VI		a	b m	3.39–3.74	58.1	388.1283	388.1278	olive-black crystals, volatile [140 °C, (10^{-3} torr)]
		b	s	7.41				
VII		a	m	4.20	34.5	412.1283	412.1293	red crystals, volatile [160 °C (10^{-3} torr)]
		b	m	4.53				
		c	s	6.68				
		d	s	6.73				
		e	m	7.10				

^{a} Varian EM-390 NMR. Multiplicity—s, singlet; m, multiplet; and b m, broad multiplet. Shift reported in ppm (δ). ^{b} Based on amount of chromium evaporated. ^{c} Analysis performed by high-resolution mass spectroscopy (Consolidated Electrodynamics Corp., Model 21-1103).

occur. We are currently engaged in the synthesis of polyhomonuclear and -heteronuclear π-arene complexes based upon IV, V, VI, and VII as precursors.

Experimental Section

The compounds reported were prepared by using a rotating reactor designed after that of Ozin[4] and Timms[3] with modifications more appropriate to our research needs. The basic design is shown in Figure 1. The rotating vacuum seal was patterned after that of Ozin using a pair of stationary, differentially pumped o-rings. A standard Büchi rotavapor R-110 drive mechanism turns a stainless-steel steam duct that was machined to a standard taper 29/42. Any round-bottom flask with the complimentary joint could be used directly on the system, thus avoiding the need for an additional o-ring seal. The electrical leads were made of $^1/_8$-in. o.d. copper tubing, cooled by continuous water flow from an inner 0.032-in. o.d. tube. Reaction flasks with capacities of 500–3000 mL may be used with the apparatus.

In a typical reaction, chromium metal is evaporated from a resistively heated, conical, tungsten basket at high vacuum directly into a 2000-mL tapered bottom rotating (approximately 35 rpm) reaction flask containing excess ligand. The flask is submerged ($^1/_3$ to $^1/_2$ its volume) in a liquid nitrogen bath (77 K). The formation of a thin orange-brown layer is observed on the inside surface of the flask almost immediately. As the reaction proceeds, the coloration gradually changes from a dark orange opaque layer to a dark brown-black opaque layer. The chromium deposition is terminated after approximately 1 h, and the reaction flask allowed to warm to room temperature under static vacuum and pressurized with dry, purified nitrogen.[6] The solid mixture is dissolved in dry, deoxygenated glyme or toluene and transferred anaerobically through a glass filter frit to remove insoluble materials and chromium metal. The solvent is then removed by flash distillation leaving a brown-black solid. Excess ligand is removed by using a Dewar condenser [77 K (10^{-3} torr)] over a period of approximately 24 h. The Dewar condenser is replaced with a water-cooled cold finger, and volatile product is removed from the nonvolatile residue and finely divided chromium metal by sublimation. The product is collected in a helium-filled drybox for further handling.

All yields reported are based on the amount of chromium metal deposited. All ligands were obtained from Aldrich and used as received.

Synthesis of Bis(η^6-durene)chromium(0) (I). Chromium metal (0.549 g, 10.6 mmol) was evaporated into durene (10.2 g, 75.8 mmol) by using a time-averaged 310 W at an average pressure of 4.6 × 10^{-5} torr during a period of 1.0 h. After transfer and workup, compound I [mp 180.5–182° C (lit.[7] mp 189–190 °C)] was collected by sublimation [59–60 °C (10^{-3} torr)]. Total yield was 0.400 g or 11.8% (HRMS calcd 320.159 60, found 320.158 99).

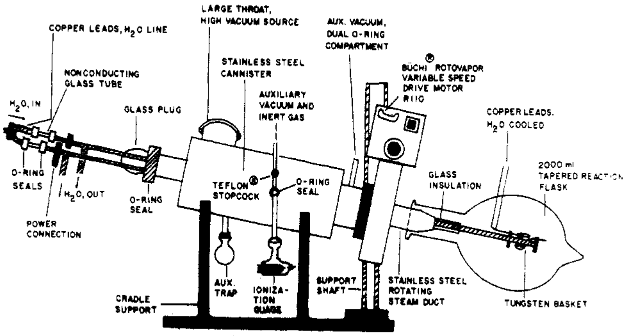


Figure 1. Rotating reactor.

Synthesis of Bis(η^6-pentamethylbenzene)chromium(0) (II). Chromium metal (0.821 g, 15.8 mmol) was evaporated into pentamethylbenene (14.1 g, 95.4 mmol) by using a time-averaged 380 W at an average pressure of 8.3 × 10^{-5} torr during a period of 1.2 h. After transfer and workup, compound II (mp 272–274 °C) was collected by sublimation [70 °C (10^{-3} torr)]. Total yield was 0.575 g or 10.4% (HRMS calcd 348.190 90, found 348,190 11).

Synthesis of Bis(η^6-hexamethylbenzene)chromium(0) (III). Chromium metal (1.11 g, 21.4 mmol) was evaporated into hexamethylbenene (10.0 g, 61.6 mmol) by using a time-averaged 360 W at an average pressure of 8.3 × 10^{-6} torr during a period of 1.0 h. After transfer and workup, compound III [mp 339–340 °C dec (lit.[8] mp 400 °C dec)] was collected by sublimation [110 °C (10^{-3} torr)]. Total yield was 0.294 g or 3.66% (HRMS calcd 376.222 20, found 376.223 13).

Synthesis of Bis(η^6-biphenyl)chromium(0) (IV) and (μ-η^6:η^6-Biphenyl)bis(η^6-biphenyl)chromium(0)] (V). Chromium metal (0.730 g, 14.0 mmol) was evaporated into biphenyl (9.6 g, 62.3 mmol) by using a time-averaged 340 W at an average pressure of 1.8 × 10^{-5} torr during a period of 1.1 h. After transfer and workup, the remaining material was collected. The mixture was separated by recrystallization.[9] Compound IV [mp 155–157 °C (lit.[10] mp 156 °C)] was then purified via sublimation [110 °C (10^{-3} torr)]. Compound V decomposes ca. 200 °C. Total yield of IV was 1.26 g or 25.0% and of V was 0.22 g or 5.6% [HRMS] ML_2^+ calcd 360.097 00, found 360.095 99, $M_2L_2^+$ calcd 412.037 514, found

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(6) Inert gasses were purified and dried by use of a standard chromium oxide on silica gel support scrubbing column.

(7) V. Graves and J. J. Lagowski, *Inorg. Chem.*, **15**, 577 (1976).

(8) E. O. Fischer and W. Hafner, Brit. Pat. 829 574, 1960.

(9) The separation and characterization of IV and V has been reported by C. Eischenbroich and J. Heck, *J. Am. Chem. Soc.*, **101**, 6773 (1979).

(10) G. E. Herberich and J. Muller, *J. Organomet. Chem.*, **16**, 111 (1969).

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412.0466 52, $M_2L_3^+$ observed by LRMS[11] only—*m/e* 566 (<1% intensity)].

Synthesis of Bis(η^6-diphenylmethane)chromium(0) (VI). Chromium metal (0.496 g, 14.0 mmol) was evaporated into diphenylmethane (15.1 g, 89.9 mmol) by using a time-averaged 350 W at an average pressure of 9.3×10^{-5} torr during a period of 1.0 h. After transfer and workup, compound VI [mp 132–133 °C (lit.[12] 132–135 °C)] was collected by sublimation [140 °C (10^{-3} torr)]. Total yield was 2.15 g or 58.1%.

Synthesis of Bis(η^6-*trans*-stilbene)chromium(0) (VII). Chromium metal (0.388 g, 7.46 mmol) was evaporated into *trans*-stilbene (13.2 g, 73.3 mmol) by using a time-averaged 310 W at an average pressure of 9.9×10^{-5} torr during a period of 1.2 h. After transfer and workup, compound VII (mp 110–113 °C) was collected by sublimation [160 °C (10^{-3} torr)]. Total yield was 1.06 g or 34.5%. No oligomerization of *trans*-stilbene was observed during the metal atom reaction.

Additional characteristics of compounds VI and VII are presented in Table I.

Results and Discussion

Our synthetic route permits the direct synthesis of bis(η^6-arene)chromium(0) compounds that are difficult to prepare by other methods. The new route eliminates the need for (a) harsh reductive solution reactions, (b) highly volatile ligands, (c) reaction solvents which must be inert to chromium atoms and have low vapor pressure at the reaction temperature and in which the ligands and/or products must be relatively soluble, and (d) the need to monitor carefully the temperature of slush baths.

We found this solvent-free synthetic route to be more efficient than the conventional method when the same compounds were prepared by both techniques in our labortory.

Our technique has also proven valuable for the synthesis of compounds IV, V, VI, and VII that will be used as precursors in future polynuclear studies. The method shows promise as a route to the formation of metal π-complexes using ligands with a low volatility and/or solubility and hence not attainable using the conventional methods.

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Registry No. I, 57820-98-1; II, 97102-75-5; III, 12156-66-0; IV, 12099-15-9; V, 72281-90-4; VI, 67775-54-6; VII, 97102-76-6; Cr, 7440-47-3; durene, 95-93-2; pentamethylbenzene, 700-12-9; hexamethylbenzene, 87-85-4; biphenyl, 92-52-4; diphenylmethane, 101-81-5; *trans*-stilbene, 103-30-0.

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(11) Low-resolution mass spectrometry performed using a Bell and Howell 21491 mass spectrometer with an ionization potential of 70 eV and a current of 7 μA.

(12) J. A. Gladysz, J. G. Fulcher, and A. B. Bocarsly, *Tetrahedron Lett.*, 20, 1725 (1978).

Theoretical and Experimental Evidence for a Thermally Induced η^4-Diene $\rightleftharpoons$ η^3-Allyl Ligand Interconversion in (*s*-*trans*-η^4-Conjugated diene)zirconocenes

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Photolysis of diphenylzirconocene (**5**) at low temperature (−50 °C) in the presence of the isomerically pure dienes (*Z,Z*)- and (*Z,E*)-2,4-hexadiene (**8a**) and (*Z,Z*)- and (*Z,E*)-1,4-diphenylbutadiene (**8b**), respectively, leads to the stereospecific formation of the corresponding (*s-trans*-η^4-conjugated diene)zirconocene complexes **1a**-*ZZ*, **1a**-*ZE*, **1b**-*ZZ*, and **1b**-*ZE*. Upon thermolysis, **1a**-*ZZ* ($\tau_{1/2} \approx 25$ min at −25 °C) first rearranges to give **1a**-*ZE* exclusively, which consecutively rearranges to a thermodynamic 60/40 mixture of **1a**-*EE*/**3a**-*EE* at higher temperature (+25 °C). Similarly, **1b**-*ZE* undergoes a thermally induced geometrical isomerization at +35 °C to form **1b**-*EE*/**3b**-*EE* (95/5). The same product mixture is obtained directly from **1b**-*ZZ* at +60 °C. The observed stepwise loss of the stereochemical information at the terminal carbon centers of the conjugated diene ligands of **1** indicates a rearrangement process proceeding through a π-allyl-type intermediate (**4**). This interpretation is supported by the result of an extended Hückel calculation: an approximate transition state (**10a′**) for a related isomerization process with an unsubstituted butadiene system can be reached by rotating this ligand around a $Zr–C_{term}$ bond (7°), lifting the exposed CH_2 group by 50°, and rotating it 90°. A barrier of 25 kcal/mol was computed. The orbitals of **10a** are in agreement with the formulation of an allyl complex. A low-lying LUMO predominantly localized at the exposed CH_2 moiety indicates carbenium ion character at this carbon. Terminal π-donor substituents at the butadiene ligand cause a drop of the rearrangement barrier to 12 kcal/mol, which can be explained by means of delocalization of carbenium p orbital character into filled wave functions of the π-donor residue. Stereochemistry and calculations have thus revealed a third general mechanistic pathway for an intramolecular diene transition-metal complex isomerization: rearrangement through π-allyl-type intermediates **4** can be of importance in addition to the established diene rotation and topomerization mechanisms.

For the interconversion of (butadiene)zirconocene isomers substantial experimental evidence has accumulated for a qualitative description of the energy profile as depicted in Figure 1.[2] The geometrical isomerization **1** $\rightleftharpoons$

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