

nochloridate **3** and starting phosphinothiolate **1** involves a second inversion at the phosphoryl center which consequentially results in retention of configuration. Racemization, instead, arises from the decomposition of the salt **7**, which leads to one molecule with unchanged configuration and another that is inverted.

It is interesting to note that in the case of the reaction involving nearly complete retention of configuration, namely, chlorination with sulfur chloride in toluene, only traces of the salt **7** are observed. In contrast, when the chlorinating agent was elemental chlorine in methylene chloride, the amount of the salt **7** observed was considerably greater, and at the same time appreciable racemization took place. Specific rotations and optical yields for chlorination reactions performed at 0 °C are included in Table I.

Participation of transient species containing two phosphorus atoms was also demonstrated in other types of organic phosphorus thioesters and will be a topic of future publications.

This communication resolves the problem of the reaction mechanism of halogenolysis of the phosphorus-sulfur bond in 4-coordinated organophosphorus compounds via the combined results of the stereochemical investigations and the structural studies accomplished by <sup>31</sup>P NMR spectroscopy of the reaction intermediates. Another important aspect of this paper is the demonstrated facile formation of the P-O-P system by nucleophilic attack of phosphoryl oxygen on the 4-coordinated phosphorus center. This result confirms the reaction schemes proposed earlier for a number of reactions, important from the synthetic point of view of the organophosphorus compounds<sup>10</sup> and polymers.<sup>11</sup>

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## Arene-Metal Complexes in Organic Synthesis: Addition to Styrene-Type Ligands

*Sir:*

The special reactivity of arene rings coordinated to transition metals has been developed into useful synthesis methodology.<sup>1</sup> An important effect is the electron-accepting power of the chromium tricarbonyl unit, which promotes nucleophilic addition to the arene ring in arene-Cr(CO)<sub>3</sub> complexes<sup>2</sup> and strongly increases the kinetic acidity of benzylic hydrogens.<sup>3</sup> Complexes of η<sup>6</sup>-styrene with Cr(CO)<sub>3</sub> have been known for many years,<sup>4</sup> and it was


(1) (a) For a recent report and leading references, see: M. F. Semmelhack and J. J. Harrison, *J. Org. Chem.*, **44**, 3275 (1979). (b) For a general review, see: G. Jaouen in "Application of Transition Metal Organometallics in Organic Synthesis", H. Alper, Ed., Academic Press, New York, Vol. 2, 1977.

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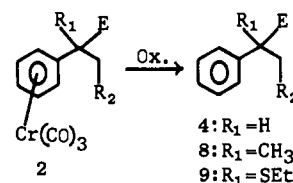
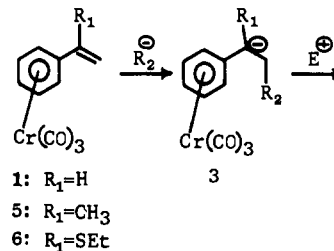
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**Table I.** Addition of Carbon Anions to Styrene-Cr(CO)<sub>3</sub> Derivatives

entry	complex	anion unit, R <sub>2</sub>	electrophile	product(s), yield, % <sup>a</sup>
1	1	-C(CH <sub>3</sub> ) <sub>2</sub> CN	H <sup>+</sup>	4: E = H, 92
2	1	-C(CH <sub>3</sub> ) <sub>2</sub> CN	CH <sub>3</sub> I	4: E = CH <sub>3</sub> , 82
3	1	-C(CH <sub>3</sub> ) <sub>2</sub> CN	CH <sub>3</sub> COCl	4: E = COCH <sub>3</sub> , 71
4	1	-(CH <sub>3</sub> ) <sub>2</sub> CO <sub>2</sub> - <i>t</i> -Bu	H <sup>+</sup>	4: E = H, 73
5	1	-C(CN)(OR)CH <sub>3</sub> <sup>c</sup>	H <sup>+</sup>	4: E = H, 75 <sup>b</sup>
6	5	-C(CH <sub>3</sub> ) <sub>2</sub> CN	H <sup>+</sup>	8: E = H, 34
7	5	-C(CN)(OR)CH <sub>3</sub> <sup>c</sup>	H <sup>+</sup>	8: E = H, 62 <sup>b</sup>
8	6	-C(CH <sub>3</sub> ) <sub>2</sub> CN	H <sup>+</sup>	9: E = H, 62
9	6	-C(CH <sub>3</sub> ) <sub>2</sub> CN	PhSSPh	9: E = SPh, 59 <sup>d</sup>
10	6	-C(CN)(OR)CH <sub>3</sub>	H <sup>+</sup>	9: E = H, 81 <sup>b,e</sup>
11	6		H <sup>+</sup>	9: E = H, 41
12	6	-C <sub>4</sub> H <sub>9</sub>	H <sup>+</sup>	9: E = H, 61
13	6	-Ph	H <sup>+</sup>	9: E = H, 84
14	6	-CH <sub>3</sub>	H <sup>+</sup>	9: E = H, 60
15	7	-C(CH <sub>3</sub> ) <sub>2</sub> CN	H <sup>+</sup>	12, 100
16	7	-C(CH <sub>3</sub> ) <sub>2</sub> CN	CH <sub>3</sub> I	14, 75
17	7	-C(CH <sub>3</sub> ) <sub>2</sub> CN	PhCOCl	15, 32

<sup>a</sup> The yield refers to isolated product after oxidation of the intermediate complexes. <sup>b</sup> The product has R<sub>2</sub> = COCH<sub>3</sub>, obtained after hydrolysis of the cyanohydrin acetal; see: G. Stork and L. Maldonado, *J. Am. Chem. Soc.*, **93**, 5286 (1971). <sup>c</sup> R = CH(CH<sub>3</sub>)OCH<sub>2</sub>CH<sub>3</sub>. <sup>d</sup> Characterized as the hydrolysis product of the bistioketal. <sup>e</sup> The product is 4-phenyl-3-buten-2-one obtained after hydrolysis of the cyanohydrin acetal and base-promoted elimination of the ethylthio group.

recognized early that nucleophilic addition to the β position of an η<sup>6</sup>-styrene ligand would generate the stabilized benzyl anion (e.g., **1**).<sup>5</sup> However, the yields of products attributed to addition



of phenyllithium (30%) and methylolithium (7%) appear to have discouraged development of this process. No simple benzyl anion coordinated to Cr(CO)<sub>3</sub> has been prepared by addition to styrene or by any other route.<sup>6</sup> We are interested in the scope and limitations of the reaction because (a) it allows conversion of a simple arene complex (e.g., **1**) into a more elaborate one (e.g., **2**), (b) it may allow isolation and study of the coordinated benzyl anion (e.g., **3**),<sup>6</sup> and (c) overall, two new carbon-carbon bonds (e.g., in **4**) could be formed, depending on the choice of nucleophile and electrophile in the reaction. We report that a variety of nucleophiles, electrophiles, and styrene-type ligands participate smoothly in the conversion represented. In the prototype example, 2-lithio-2-methylpropionitrile added to η<sup>6</sup>-styrenechromium tricarbonyl slowly at -30 °C in THF, and quenching with ammo-

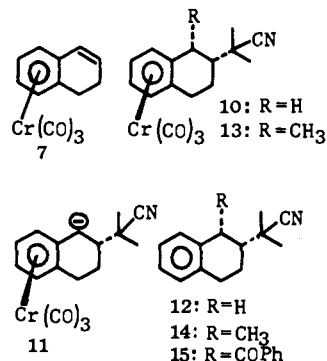
(5) G. R. Knox, D. G. Leppard, P. L. Pauson, and W. E. Watts, *J. Organomet. Chem.*, **34**, 347 (1972).

(6) Related species have been characterized, but simple benzyl anions on Cr(CO)<sub>3</sub> have not been observed directly. For related examples, see: J. F. Helling and W. A. Hendrickson, *J. Organomet. Chem.*, **141**, 99 (1977). For species such as **3** as transient intermediates, see ref 3.

nium chloride (aqueous) after 3 h, produced complex **2** [ $R_1 = C(CH_3)_2CN$ ,  $E = H$ ] in 92% yield.

The results with four styrene complexes (**1**, **5**, **6**, and **7**) are summarized in Table I. The complexes were prepared by direct complexation of the styrene with chromium hexacarbonyl according to standard procedure (for **1**,<sup>4</sup> **6**,<sup>7</sup> and **7**<sup>8</sup>), or by an indirect procedure involving metalation of benzenechromium tricarbonyl, reaction with acetone, and elimination of water (for **5**).<sup>9,10</sup> The general procedure for nucleophilic addition/electrophilic trapping involved adding the styrene complex to a solution of the nucleophile in tetrahydrofuran at  $-78^\circ C$  and allowing the mixture to warm to 0 or  $25^\circ C$ ; then the electrophile was added, producing a stable complex (i.e., **2**) which was generally decomposed in excess iodine or ceric ammonium nitrate to afford the free arene. The anion of diethyl malonate failed to add to **1** while the lithium enolate anion from *tert*-butylmethyl ketone gave 10% of the expected adduct and no other products. With 2-lithio-1,3-dithiane, reaction with **1**, **5**, and **7** occurred, but the simple products from addition to the styrene terminus were not detected; however, the dithiane anion and other organolithium reagents add reasonably well to the  $\alpha$ -(ethylthio)styrene complex (**6**, entries 11–14). The intermediate benzyl anions (**3**) are currently under study; the simple example of **3** with  $R_1 = H$  and  $R_2 = C(CH_3)_2CN$  is stable at  $25^\circ C$  for many hours. The  $\alpha$ -methyl substituent in **5** led to somewhat lower efficiency in the overall process (entries 7 and 8), but it is not yet clear whether this is due to kinetic or thermodynamic effects. The  $\alpha$ -(ethylthio) substituent has a beneficial effect in general.

The dihydronaphthalene complex **7** provides an example of the excellent stereochemical control in reactions of rings fused to arene- $Cr(CO)_3$  complexes.<sup>12</sup> Reaction with 2-lithio-2-methylpropionitrile proceeded rapidly at  $0^\circ C$ ; addition of saturated aqueous ammonium chloride solution followed by oxidative decomposition with ceric ammonium nitrate solution gave the adduct **12** as a colorless oil in 95–100% yield after short-path distillation [ $50^\circ C$  (0.001 torr)]. The intermediate complex **10** [ $E = H$ ,  $R$



$= C(CH_3)_2CN$ ] can be isolated before the oxidation step, as a yellow solid with mp  $158$ – $159^\circ C$ , in 81% yield. Reaction of a solution of anion **11** with excess methyl iodide at  $-78^\circ C$  (warming slowly to  $0^\circ C$  over 0.5 h) produced a mixture of complexes **7**,

(7) Complex **6** was prepared by heating  $\alpha$ -(ethylthio)styrene with chromium hexacarbonyl in dioxane at reflux under argon with an air condenser.<sup>2</sup> It was characterized by  $^1H$  NMR, IR, mass spectroscopy, and combustion analyses (Supplementary Material).

(8) Complex **7** was obtained in 78% yield by heating 1,2-dihydronaphthalene with chromium hexacarbonyl in dioxane at reflux under argon for 40 h with an air condenser. It was recrystallized from a mixture of ether/hexane to give yellow crystals of mp  $107$ – $108^\circ C$ . The only previous literature report described an oil: H. Falk, K. Schlogel, and W. Steyer, *Monatsh. Chem.*, **97**, 1029 (1966). Full characterization appears in the supplementary material.

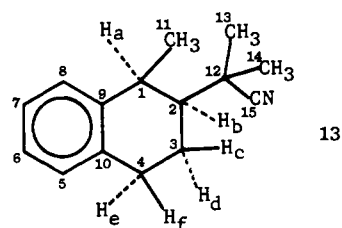
(9) Complex **5** has been obtained by direct reaction of  $\alpha$ -methylstyrene with chromium hexacarbonyl, but the indirect procedure<sup>10</sup> is generally more efficient (yields of 95–98%) for substituted styrene complexes.

(10) M. F. Semmelhack, J. Bisaha, and M. Czarny, *J. Am. Chem. Soc.*, **101**, 768 (1979).

(11) For an earlier characterization of complex **5**, see: (a) R. C. Pruet, J. E. Wyman, D. R. Rink, and L. Parts, U.S. Patent 3 378 589; (b) *Chem. Abstr.*, **69**, 77512 (1968).

(12) For examples, see: M. A. Boudeville and H. des Abbayes, *Tetrahedron Lett.*, 2727 (1975).

**10**, and **13** in a ratio of 1:2:6. Complete separation of **10** and

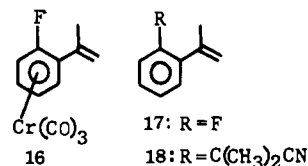


**13** by chromatography was not achieved, but oxidation of the mixture followed by chromatographic purification provided the 1,2-disubstituted tetralin **14** as a colorless oil in 65% yield. The product is homogeneous (TLC,  $^{13}C$  NMR) and is assigned the *cis* orientation, based on detailed analysis of the  $^1H$  NMR spectral data,<sup>13</sup> and the well-established tendency for *exo* attack in the reactions of rigid bicyclic arene- $Cr(CO)_3$  complexes.<sup>12</sup>

Further studies on **10** and **11** brought out limitations which may have general significance. Trapping of **11** with benzoyl chloride afforded an adduct (after oxidation) in only 32% yield which is assigned structure **15** (stereochemistry not determined), and other carbon electrophiles were less successful. Acetyl chloride, for example, gave only **10** in high yield under a variety of conditions, presumably via proton delivery. Formaldehyde and chloromethyl methyl ether gave low yields (<15%) of the expected adducts. The efficiency of reaction with methyl iodide was unexpectedly dependent on reaction temperature. When methyl iodide was added to a solution of **4** at  $25^\circ C$ , rapid reaction ensued to produce 2,2-dimethylpropionitrile and the starting complex, **7**. Reaction at  $0^\circ C$  gave a 1:1 mixture of **10** and **13**. We interpret these results in terms of a mobile equilibrium between **7** and **11** in the presence of  $LiC(CH_3)_2CN$ , heavily favoring **11** (essentially quantitative formation of **12** by quenching with ammonium chloride at  $-78$ ,  $0$ , and  $25^\circ C$ ). Then at  $-78^\circ C$ , reaction of the equilibrium mixture favored methylation of **11** (to give **13**) while at  $25^\circ C$  the reverse reaction was fast enough to allow selective methylation of  $LiC(CH_3)_2CN$  (to regenerate **2**).

Reactions of **7** with certain carbon nucleophiles gave results which are not well understood. For example, *tert*-butyl lithioacetate was mixed with **7** in a 1:1 mixture of THF/HMPA, quenched with aqueous ammonium chloride, and oxidized with ceric ammonium nitrate, to give a dimer of dihydronaphthalene as the major product (>90% yield). The same product was obtained (88% yield) by using  $LiCH_2SOPh$ . Work is in progress to define this process.

The complex **16** of *o*-(2-propenyl)fluorobenzene (**17**) was prepared by the sequence metalation of (fluorobenzene)chromium tricarbonyl,<sup>10</sup> quenching with acetone, and acid-promoted de-



hydration. Reaction of **16** with  $LiC(CH_3)_2CN$  occurred slowly. Quenching with ammonium chloride after 2.5 h at  $0^\circ C$  followed by ceric oxidation produced **17** (90% recovery), but after reaction for 5 h at  $25^\circ C$  the quenching procedure gave **18** in 76% yield. No evidence for addition to the olefin unit was obtained.

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(13) The evidence for the *cis* stereochemistry in **14** rests primarily on a coupling constant of 4.0 Hz for the protons at C-1 and C-2. Inspection of molecular models indicates that the reasonable conformation for the corresponding *trans* isomer would show a coupling larger than 7 Hz for the same protons, using the Karplus relation for vicinal proton-proton coupling.

