Table VIII. Comparison between Intuitively Predicted Qualitative and Calculated Oxidizer Strengths for Fluorides and Oxyfluorides of Chlorine and Xenon

predicted order		calculated order		
oxidation state	species	oxidation state	species	FPD value (kcal/mol)
+VII	ClF_6^+	+VII	ClF_4O^+	135.6
+VII	ClF_4O^+	+VII	ClF_6^+	147.3
+VII, +V	$ClF_2O_2^+$, ClF_4^+	+V	ClF_4^+	158.7
+V	ClF_2O^+	+VII	$ClF_2O_2^+$	161.0
+III	ClF_2^+	+III	ClF_2^+	167.1
+I	Cl_2F^+	+I	Cl_2F^+	179.1
		+V	ClF_2O^+	193.0
+VIII	XeF_7^+	+VIII	XeF_7^+	116.7
+VIII	XeF_5O^+	+VIII	XeF_5O^+	139.8
+VIII, +VI	$XeF_3O_2^+$, XeF_5^+	+VIII	$XeF_3O_2^+$	141.7
+VI	XeF_3O^+	+IV	XeF_3^+	152.4
+VI, +IV	$XeFO_2^+$, XeF_3^+	+VI	XeF_5^+	158.9
+IV	$XeFO^+$	+II	XeF^+	164.8
+II	XeF^+	+VI	XeF_3O^+	173.1
		+IV	$XeFO^+$	182.4
		+VI	$XeFO_2^+$	195.3

fluorine ligands are replaced by one doubly bonded oxygen ligand. Therefore, the formal oxidation state of the central atom remains the same but its coordination number is decreased by one. Since the formal oxidation state does not change, the number of free valence electron pairs on the central atom also remains constant. Hence, a study of the trends of the FPD values in fluorine–oxygen exchange reactions is ideally suited for the elimination of the strong effect exercised by a change in the number of free valence electron pairs (see above) and for an analysis of the influence caused by a change in the coordination numbers, i.e., of steric effects. In the absence of any steric effects, the oxidizing strength should monotonically decrease (i.e., the FPD values increase) with the stepwise replacement of two fluorines by one oxygen. Inspection of Table VII, however, clearly shows that the FPD values do not change monotonically, and that pseudooctahedral and pseudotetrahedral species are considerably weaker oxidizers than pseudo-pentagonal-bipyramidal, pseudo-trigonal-bipyramidal, and pseudo-trigonal-planar species. This effect is most pronounced for the transitions from the $HalF_6^+$ to the $HalF_4O^+$ cations. Instead of increasing FPD values, they exhibit a systematic decrease by about 11 kcal mol^{-1}. The surprising implication that $HalF_4O^+$ cations are significantly stronger oxidizers than the corresponding $HalF_6^+$ cations is in accord with our past experimental failures to synthesize these $HalF_4O^+$ cations.

Conclusions

Local density functional calculations are well-suited for the calculation of the geometries and relative energies of oxidative fluorinators. The oxidizing strength of oxidative fluorinators is determined by their F^+ detachment energies. A relative scale of FPD values can be obtained from the LDF calculations and can be converted to an absolute scale by the choice of a suitable zero point (FPD of $F^+ \equiv 0$) and an experimentally known FPD value (KrF^+ in this study).

An analysis of the oxidizer strengths, calculated in the above manner for 36 oxidative fluorinators, shows that the results are self-consistent and exhibit some expected, but also some highly unexpected features. Obviously, the oxidizing strength is governed to a large extent by the oxidation state and electronegativity of the central atom and the fact that the contribution of one doubly bonded oxygen is less than that of two singly bonded fluorine ligands. Among the less expected features are the following: (i) the presence of one or more free valence electron pairs on the central atom strongly decreases the oxidizing strength of a species, and (ii) the oxidizer strengths of pseudooctahedral and -tetrahedral species are depressed relative to those of pseudopentagonal or -trigonal-bipyramidal and -trigonal-planar ions. Thus, a simplistic picture is inadequate, that is, that the oxidizer strength should be governed exclusively by the oxidation state of the central atom and that, in case of similar values between a binary fluorine and oxyfluorides, the species with the larger number of fluorine ligands will be the stronger oxidizer. This is demonstrated by Table VIII, which shows a comparison between intuitive qualitative predictions and the quantitative results from our calculations for the fluorides and oxyfluorides of chlorine and xenon. For the chlorine compounds, the top placement of ClF_4O^+ and last placement of ClF_2O^+ are highly unexpected. Similarly, the last rank of $XeFO_2^+$ and the position of XeF_5^+ below XeF_3^+ and the high ranking of XeF^+ are a total surprise, but can be understood on the basis of the above analysis.

The availability of a quantitative oxidizer strength scale is expected to significantly contribute to our understanding of oxidizer chemistry and to the future syntheses of novel and known oxidative fluorinators. It also stresses the importance of employing high activation energy sources such as discharges or plasmas to generate intermediate F^+ cations, if novel oxidizers are desired which are more powerful than KrF^+.

Acknowledgment. The work at Rocketdyne was financially supported by both the U.S. Army Research Office and the Air Force Phillips Laboratories. K. Dobbs (du Pont) is thanked for help in performing some of the calculations.

A Protective Strategy in Carbene Complex Chemistry. Synthesis of Functionalized Fischer Carbene Complexes via Dianion Formation

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Abstract: Anionic derivatives of Fischer-type carbene complexes (A and B) are stable toward strong bases and nucleophiles, and their organic moieties R and R^2 can be elaborated under strongly basic conditions to provide access to heteroaromatic and aliphatic carbene complexes bearing organic functional groups. The concept of anionic protection has been illustrated by the reactions of dianions **9** and **14** and the preparation of carbene complexes possessing up to four chiral centers. Some attempts to effect ortho lithiation of aromatic carbene complexes are also described.

Despite the importance of Fischer carbene complexes for the development of novel organic transformations,[1] there are still a very limited number of basic repertoires for the synthesis of complexes possessing elaborate organic functional groups.[2] This

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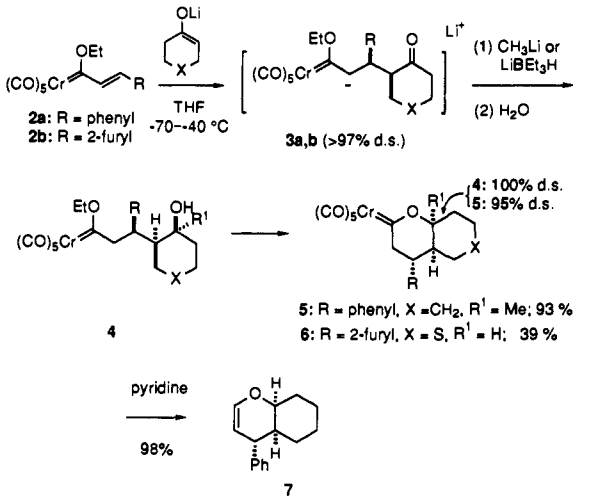
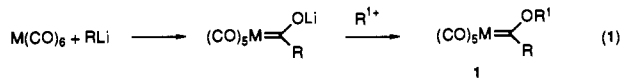
Scheme I



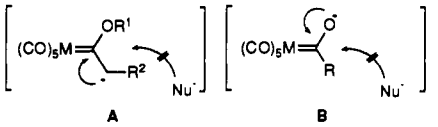
often represents a bottleneck for their organic applications. Preparation of a Fischer carbene complex of a group 6 metal (**1**) generally involves two steps: addition of an alkyllithium (RLi) to a metal carbonyl, followed by conversion of the resulting anionic complex to the corresponding alkoxy complex (eq 1). The in-



(1)

trinsically small range of the functional groups available on the lithium alkyl part imposes the first limitation to the organic residue. In addition, high susceptibility of the carbene carbon to nucleophilic attacks[3] makes it difficult to elaborate the organic moiety under basic conditions (e.g., with RLi or amide bases) in a way that organic chemists routinely carry out standard transformations.[4] It was felt that a method to attenuate the electrophilicity of the carbene carbon, namely, protection,[5] would bring in a conceptual advance to the synthetic chemistry of carbene complexes.

We report here a general strategy for temporary "protection" of the carbene complex toward nucleophilic attacks through anion formation adjacent to the carbene carbon (i.e., A and B). We demonstrate the utility of the new approach with two examples—first, with the aid of the carbon anion A,[6] the preparation of aliphatic carbene complexes with many elements of stereochemistry and functional groups, and second, the preparation of functionalized heteroaromatic carbene complexes with the oxygen anion B.[7] Attempted ortho lithiation of arylcarbene complexes will also be described briefly.



Results and Discussion

The Carbon Anion Approach. In our first approach, by taking the keto anion **3** as an example, we probed the stability of the carbon anion A derived from an aliphatic carbene complex against a strong nucleophile or a base. The method permitted the synthesis of highly elaborate aliphatic carbene complexes. We examined first the stability of the anion toward a strong nucleophile (Scheme I). To this end, we prepared in situ the anion **3** (X = CH_2) by highly syn-selective (>97% ds) Michael addition[8] that we found recently.[9] Thus, cyclohexanone lithium enolate was added to **2a** at −70 °C in THF, and the anion **3a** was treated with MeLi (3 equiv). The reaction took place exclusively at the ketone group to afford the adduct **4** (X = CH_2, R = Me), which spontaneously underwent intramolecular alkoxy exchange[8b,10] to give bicyclic complex **5** in 93% isolated yield (based on **2a**) as a single isomer. Similarly, in a sequence of the reactions starting from 4-thiacyclohexanone and **2b**, reduction of the ketone group in **3b** (X = S, R = 2-furyl) with $LiBEt_3H$ proceeded chemo- and stereoselectively to give **6** with 95% ds in 39% overall yield. Further transformation of the bicyclic compound **5** to the enol ether **7** (pyridine 98%)[11] illustrates the strategic utility of the protection concept in organic synthesis.

Next, we examined the action of a base on A to generate a dianionic species (eq 2). Thus, treatment of **8a** with 2 equiv of lithium diisopropylamide (LDA) at −70 °C in THF generated **9a** (X = CH_2), which reacted with benzaldehyde exclusively on the enolate moiety to give **10a**.[12] The simple diastereoselectivity of the aldol reaction (threo)[13] and the stereochemistry with respect to the cyclohexane ring[14] are in accordance with the precedents. The highly stereoselective Michael and aldol reactions created the chiral centers in **10a** with a ratio of **10a** and two other minor isomers of about 90:5:5. Similarly, in the 4-thiacyclohexanone series, **9b** reacted with benzaldehyde to afford **10b** of ca. 90%

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(5) Despite the known analogy between a carbene complex and a carbonyl group (especially as an electron-withdrawing group, cf. ref 1d), the latter merits from a vast collection of protecting groups, while the former suffers from the total lack of them.

(6) For the structure of "carbon anion", see: Casey, C. P.; Anderson, R. J. *J. Am. Chem. Soc.* **1974**, *96*, 1230.

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(9) Such Michael additions are generally syn selective: manuscript in preparation.

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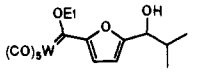
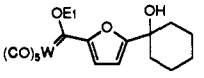
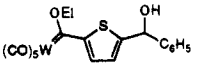
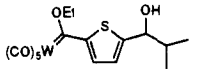
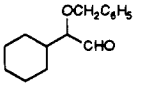
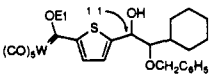
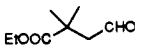
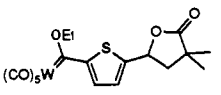
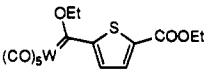
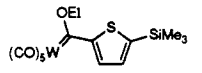
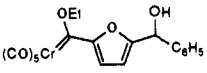
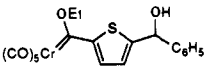
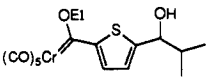
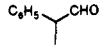
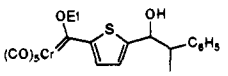
(11) Fischer, E. O.; Plabst, D. *Chem. Ber.* **1974**, *107*, 3326.

(12) Cf.: Wulff, W. D.; Gilbertson, S. R. *J. Am. Chem. Soc.* **1985**, *107*, 503.

(13) Cf.: Yamago, S.; Machii, D.; Nakamura, E. *J. Org. Chem.* **1991**, *56*, 2098 and references therein.

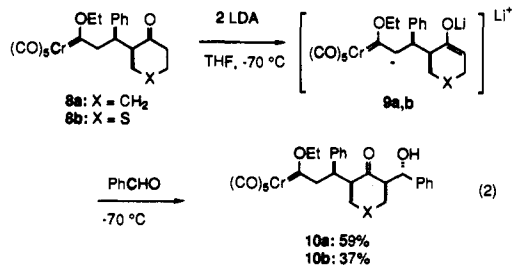
(14) Cf.: House, H. O.; Crumrine, D. S.; Teranishi, A. Y.; Olmstead, H. D. *J. Am. Chem. Soc.* **1973**, *95*, 3310. See also: Nakamura, E.; Shimizu, M.; Kuwajima, I.; Sakata, J.; Yokoyama, K.; Noyori, R. *J. Org. Chem.* **1983**, *48*, 932.

Table I. Preparation of Substituted Furyl and Thienyl Carbene Complexes

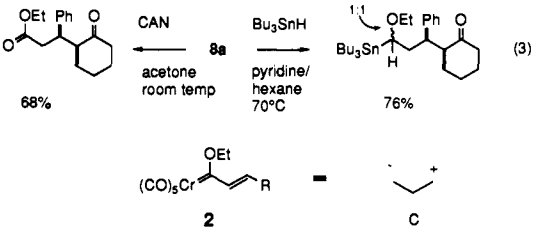
entry	M	X	electrophile	product	% yield[a]
1	W	O			79
2	W	O			27
3	W	S	C_6H_5CHO		61
4	W	S			89
5	W	S			65
6	W	S			48
7	W	S	ClCOOEt		60
8	W	S	Me_3SiCl		63
9	Cr	O	C_6H_5CHO		69
10	Cr	S	C_6H_5CHO		62
11	Cr	S			64
12	Cr	S			87

[a] Isolated yield.

stereochemical purity which possesses four chiral centers on its latent acyclic carbon backbone.[15]

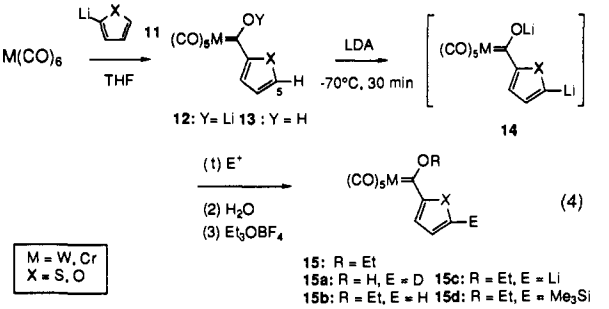


To briefly illustrate the utility of these carbene complexes in organic synthesis, we show two examples of chemoselective transformations depicted in eq 3. First, the ketonic complex **8a** was converted with ceric ammonium nitrate (CAN) to the corresponding keto ester.[2g,16] It may be noted that the reaction of an enolate with **2** represents an equivalent of the Michael addition of a ketone enolate to an α,β-unsaturated ester,[17] which is a generally difficult reaction. Another useful transformation is the conversion of the carbene moiety in **8a** to an α-alkoxytin group (76% yield).[18] The reaction conditions are mild enough to keep the ketone group intact. This operation transforms the electrophilic carbenic carbon to a potential nucleophilic center.[19] By this token, the unsaturated carbene complex **2** serves as a 1,3-dipole synthon C.



The Oxygen Anion Approach. For carbene complexes lacking the acidic α-protons, we probed the use of the oxygen anion **B**, which is a direct precursor of alkoxycarbene complexes.[20] We examined our protective protocol for the dianion formation from a heteroaromatic carbene complex possessing a relatively acidic hydrogen.

The chemistry is illustrated in eq 4 for the generation of the dianion **14** from the anion **12**. To examine the feasibility of the approach, we treated the hydroxycarbene complex **13** (X = S, M = W) with 2.4 equiv of LDA at −70 °C for 30 min in THF, then with D_2O, and finally with dilute aqueous HCl to acidify the mixture. The reaction gave back 50% of **13** with 100% deuterium incorporation at C(5) (**15a**),[21] indicating the formation of the dianion **14**. Trapping of **14** could also be achieved in excellent yield with a carbon electrophile: addition of 1.2 equiv of benzaldehyde and quenching with a small amount of water, followed by ethylation with Meerwein salt, afforded the adduct **15** (R = Et, E = CH(OH)Ph) in 87% isolated yield.



Many attempts to generate and trap the corresponding monoanion **15c** (R = Et, E = Li) from the alkoxy complex **15b** (R = Et, E = H; X = S, M = W for all experiments in this paragraph) failed under a variety of conditions (LDA, lithium tetramethylpiperidide (LiTMP), *n*-BuLi under various conditions related to those applied for the dianion generation). However, the unstable monoanion **15c** may only be generated at low temperature and immediately trapped in situ with an electrophile. Thus, deprotonation of **15b** with LiTMP *in the presence* of Me_3SiCl afforded **15d** in 55% yield.

The dianion formation/trapping sequence operates equally well with thienyl and furyl (X = O) complexes[22,23] in both tungsten

(15) 4-Thiacyclohexanone serves as a latent diethyl ketone of fixed conformation: Hayashi, T. *Tetrahedron Lett.* **1991**, *32*, 5369 and references therein. See also: Nógrádi, M. *Stereoselective Synthesis*; VCH: Weinheim, 1987.

(16) Casey, C. P.; Boggs, R. A.; Anderson, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 8947.

(17) It may be noted that the diastereoselectivity is opposite to that in the conventional Michael addition (cf.: Heathcock, C. H.; Norman, M. H.; Uehling, D. E. *J. Am. Chem. Soc.* **1985**, *107*, 2797).

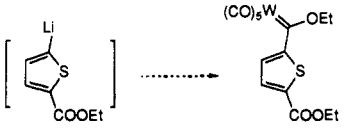
(18) (a) Connor, J. A.; Rose, P. D.; Turner, R. M. *J. Organomet. Chem.* **1973**, *55*, 111. (b) No diastereoselectivity was observed in the Sn–H bond insertion.

(19) (a) Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1481. (b) Sawyer, J. S.; Macdonald, T. L.; McGarvey, G. J. *J. Am. Chem. Soc.* **1984**, *106*, 3376.

(20) B itself has recently been shown to be a useful synthetic intermediate: Hoye, T. R.; Rehberg, G. M. *J. Am. Chem. Soc.* **1990**, *112*, 2841.

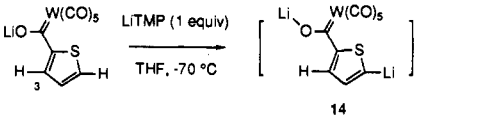
(21) The moderate yield is due to the instability of the hydroxy complex **13**.

and chromium series. Practically, it is unnecessary to deals with the unstable hydroxy complex **13**. Thus, **15** was prepared in a single pot (eq 4) by treatment of $M(CO)_6$ with a suitable lithium reagent (**11**) followed by sequential addition of LDA, an electrophile (E^+), water, and finally Meerwein salt or $MeOSO_2F$. The results are summarized in Table I, wherein the yields refer to the overall yield of the one-pot five-step sequence. The virtue of the present reaction sequence is demonstrated in the preparation of carbene complexes bearing base-sensitive groups (e.g., lactone and ester) on their organic moiety (entries 6 and 7). The synthesis of **17** (entry 7) by a conventional method, for instance, would call for the use of an unstable lithium reagent **16**.

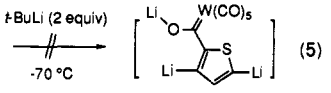


16 17

Attempts to prepare the trianion **18** (directed lithiation) by treatment of the dianion **14** with *sec*-butyllithium (eq 5, followed by Me_3SiCl quenching) resulted only in the formation of the C(5)-monosilylated compound **15d** (E = Me_3Si) in 52% yield, only to provide further evidence of the base stability of the anionic carbene functionality.[24] In no cases could we find evidence for the desired ortho lithiation (i.e., deprotonation at the C(3) position of the thiophene ring).[25]



14

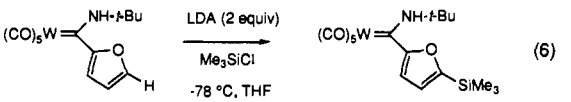


(5)

18

The conditions used for the formation of oxygen dianion **14** fail to dilithiate the aminocarbene complex **19** and gave back the starting material, leading to two conclusion: inability of a base to generate a dianion of an aminocarbene complex and the base stability of the aminocarbene complex. However, treatment of **19** with LDA *in the presence* of Me_3SiCl (eq 6) afforded the silylated product **20** in 22% yield (together with the starting material, 67%): the formation of **20** may involve the formation of C(5) monolithiated *N*-silyl compound.

Attempted Carbene-Directed Lithiation. Literature provides numerous examples of (lithiated) secondary amide and tertiary amide facilitating ortho lithiation[26] through electron-withdrawing

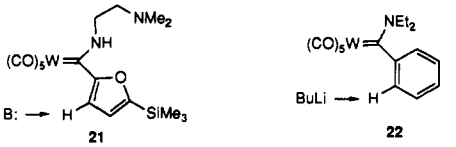


(6)

19 20 (22%)

and complex-induced proximity effects.[27] We envisioned that an aminocarbene group[28] attached to an aromatic group may facilitate lithiation of the aromatic ortho-proton, because of its (probable) electron-withdrawing ability as well as possible coordination ability.

Against our expectation, attempts to effect ortho lithiation of **20–23** uniformly failed under various conditions described in the literature[26] and gave back the starting material (60–100%), which in turn attests to their base stability. In no case could we find evidence for the formation of dianions.



21 22

base: n-BuLi/hexane; n-BuLi/ether; n-BuLi/TMEDA/ether;

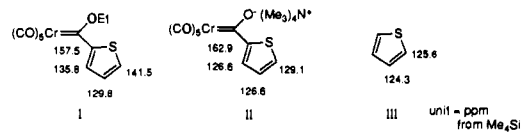
Several lines of evidence suggest that the anionic carbene or aminocarbene moiety may even retard ortho lithiation. The carbene complex **23** has a proton flanked by the carbene moiety and a methoxy group. The effect of the methoxy group is strong enough to lithiate the adjacent aromatic proton (cf. the second equation in Scheme II). However, the reaction of **23** with a variety of strong bases resulted in nearly quantitative recovery of the starting material, suggesting that the carbene moiety suppresses ortho lithiation. In conclusion, these sets of experiments gave negative evidence for the ortho-directing ability of aminocarbene groups.[29]

Conclusion. The present studies have shown that a variety of functionalized Fischer carbene complexes become available by attenuating the electrophilicity of carbene complexes by placing an anionic charge adjacent to the carbene carbon. Given the simplicity of the concept and the procedure, we expect that "anionic protection" of the reactive carbene carbon against nu-

(22) For the reactions of thienyl and furyl complexes; see: (a) Dötz, K. H.; Dietz, R. *Chem. Ber.* **1978**, *111*, 2517. (b) Yamashita, A.; Scahill, T. A. *Tetrahedron Lett.* **1982**, *23*, 3765. (c) Yamashita, A. *J. Am. Chem. Soc.* **1985**, *107*, 5823. (d) Wulff, W. D.; McCallum, J. S.; Kunng, F.-A. *J. Am. Chem. Soc.* **1988**, *110*, 7419. (e) Yamashita, A. *Tetrahedron Lett.* **1988**, *29*, 3403. (f) Yamashita, A.; Toy, A.; Ghazal, N. B.; Muchmore, C. R. *J. Org. Chem.* **1989**, *54*, 4481.

(23) The corresponding pyrrole carbene could not be deprotonated because of the low acidify of its C-5 proton; cf.: Gschwend, H. W.; Rodrigues, H. R. *Org. React.* (*N.Y.*) **1979**, *26*, 21.

(24) It is likely that here the anionic carbene moiety no longer acts as an electron-withdrawing group. For instance, the rather normal ^{13}C NMR chemical shift of the C(5) furyl carbon of ii (cf. iii) makes a strong contrast with the downfield shift of the same carbon in i. See also ref 29.



I II III

The data were taken from the following: Connor, J. A.; Jones, E. M.; Randall, E. W.; Rosenberg, E. *J. Chem. Soc. A* **1972**, 2419.

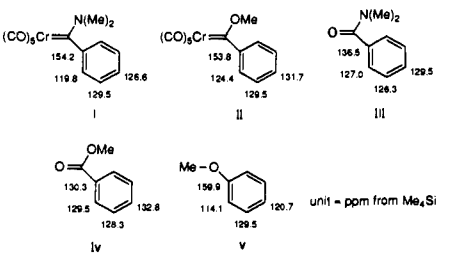
(25) For the regiochemistry of lithiation of thiophenes substituted by potentional ortho-directing groups, see: Graham, S. L.; Scholz, T. H. *J. Org. Chem.* **1991**, *56*, 4260.

(26) (a) Geschwend, H. W.; Rodriguez, H. R. *Org. React.* (*N.Y.*) **1979**, *26*, 1. (b) Klumpp, G. W. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 1. Beak, P.; Snieckus, V. *Acc. Chem. Res.* **1982**, *15*, 306.

(27) (a) Beak, P.; Meyers, A. I. *Acc. Chem. Res.* **1986**, *19*, 356. (b) For the excellent experimental and theoretical work, see: Bauer, W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1989**, *111*, 7191.

(28) For the synthetic utility of aminocarbene complexes, see: Grotjahn, D. B.; Dötz, K. H. *Synlett* **1991**, 381.

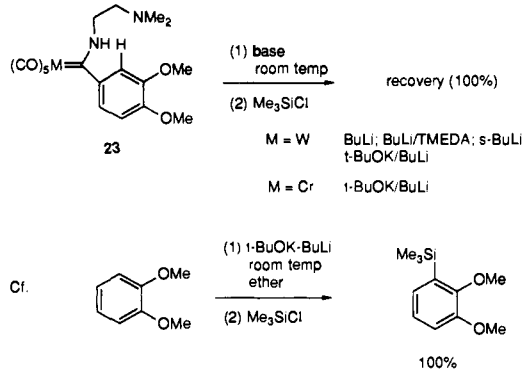
(29) The ^{13}C NMR spectra may provide useful information relevant to this conclusion, while they are not necessarily a reliable measure of electron density on carbon. The strong inductive effect of the carbene moiety causes significant downfield shift of the ipso carbon (i and ii) as with iii and iv. On the other hand the ortho- and para-carbon of i (known to be subject to the resonance effect) experience an upfield shift (cf. benzene, 128.5 ppm), suggesting that the aminocarbene group mesomerically *donates* electron to the aromatic ring (as with benzylic metal compounds). The similarity of the chemical shifts of i and of aniosol v may not be a mere coincidence. Spectra of vinyl carbene complexes also show a similar trend (Wilson, J. W.; Fischer, E. O. *J. Organomet. Chem.* **1973**, *57*, C63). In this respect, it is interesting to note that, in crystals, the metal–carbene bond is orthogonal to the plane of the pheny or the vinyl groups (ref 1a).



I II III IV V

The data for the carbene complexes were taken from Connor, J. A.; Jones, E. M.; Randall, E. W.; Rosenberg, E. *J. Chem. Soc. A* **1972**, 2419, and others from Breitmaier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy*; VCH: Weinheim, 1987.

Scheme II



cleophilic attack would prove readily applicable to a variety of compounds. In addition, given the established importance of dianions in carbonyl chemistry, we expect that the polyanions will have high potential as a reactive species in carbene complex chemistry. In addition, the temporary protection of the potential reactive site may also find use for the functionalization of other transition metal complexes, and for the strategic assemblage of metal complexes aiming at the design of functional materials.

Experimental Section

General. Routine chromatography was carried out on silica gel using hexane/AcOEt as eluent. ^1H NMR (200, 270, and 500 MHz) and ^{13}C NMR (50, 67.5, and 125 MHz) spectra were measured for a $CDCl_3$ solution of a sample on JEOL FX-200, GSX-270, and GSX-500 instruments, respectively. ^1H NMR spectra are reported in parts per million from internal tetramethylsilane, and ^{13}C NMR spectra from $CDCl_3$ (77.0 ppm). IR spectra were recorded on a JASCO IR-800; absorptions were reported in cm^{-1}. THF was distilled from sodium benzophenone ketyl immediately before use.

The Carbon Anion Approach, Cyclization. Preparation of Bicyclic Carbene Complex 6. To a solution of 1-(trimethylsiloxy)-4-thiacyclohexene (217 μL, 1.2 mmol) in 2 mL of THF was added 1.64 M BuLi in hexane (0.73 mL, 1.2 mmol) at 0 °C. After 40 min the mixture was cooled to −70 °C and transferred to a solution of **2b** (342 mg, 1.0 mmol) in 2 mL of THF at −70 °C. The reaction mixture was warmed to −10 to −40 °C for 30 min and then cooled to −70 °C again. A 1.0 M solution of $LiBEt_3H$ in THF (1.5 mL, 1.5 mmol) was added to the mixture, and, after 1 h, 100 μL of H_2O was added. The mixture was warmed to 0 °C, poured into 20 mL of hexane, washed five times with 5 mL of H_2O, and finally dried over $MgSO_4$. Solvent was removed, and the residue was purified on silica gel (5–20% AcOEt in hexane) to give 156 mg of **6** (39%): IR (CCl_4) 2035, 1945, 1245, 1225, 1020, 665; ^1H NMR (270 MHz, $CDCl_3$) 7.36 (d, J = 2.0 Hz, 1 H), 6.32 (dd, J = 2.0, 3.4 Hz, 1 H), 6.10 (d, J = 3.4 Hz, 1 H), 4.71–4.78 (m, $J_{1/2}$ = 9 Hz, 1 H), 4.39 (dd, J = 6.4, 16.6 Hz, 1 H), 3.17 (ddd, J = 2.4, 12.2, 14.2 Hz, 1 H), 3.04 (dd, J = 9.8, 16.6 Hz, 1 H), 2.68–2.82 (m, 2 H), 2.4–2.6 (m, 4 H), 2.19 (dddd, J = 2.4, 3.9, 12.2, 14.7 Hz, 1 H). Anal. Calcd for $C_{17}H_{14}O_7SCr$: C, 49.28; H, 3.41. Found: C, 49.36; 3.53.

The narrow width of the broad signal at δ 4.71–4.78 indicated the equatorial disposition of this methyne proton connected to the carbenic oxygen atom, which in turn indicates cis-fusion of the two rings. This stereochemistry indicates that the hydride reduction of the cyclohexanone carbonyl in **2** took place from the less hindered side as expected.

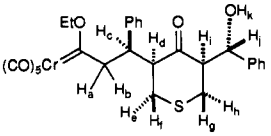
Bicyclic Carbene Complex 5. Prepared from **2a**, cyclohexanone lithium enolate, and methyllithium in the same manner as described for **6** on a 0.1-mmol scale in 93% yield (38.9 mg): IR (CCl_4) 2950, 1990 (w), 1960 (vs), 1260, 1240, 1040, 980, 700, 670, 660, 460; ^1H NMR (200 MHz, $CDCl_3$) 7.2–7.6 (m, 3 H), 6.9–7.2 (m, 2 H), 4.04 (m, 2 H), 2.60 (dt, J = 7.6, 12.4 Hz, 1 H), 2.40 (br d, J = 12.4 Hz, 1 H), 1.47 (s, 3 H), 0.7–2.0 (m, 8 H). Anal. Calcd for $C_{21}H_{20}O_6Cr$: C, 60.00; H, 4.80. Found: C, 60.10; H, 4.95.

CH Insertion Reaction of 5. Preparation of Enol Ether 7. Pyridine (73 μL, 0.9 mmol) was added to a solution of the complex **5** (63 mg, 0.15 mmol) in 0.3 mL of hexane. The mixture was stirred at 60 °C for 2.5 h. After removal of the solvent, chromatographic purification (SiO_2, EtOAc/hexane, 95:5) gave the enol ether **7** (31.2 mg, 98%): IR (neat) 2950, 1655, 1450, 1250, 1100, 1060, 755, 750, 700; ^1H NMR (200 MHz, $CDCl_3$) 1.06–1.80 (m, 8 H), 1.80–2.06 (m, 1 H), 3.06 (br d, 1 H, J = 4.8 Hz), 3.90 (br t, 1 H, J = 1.9 Hz), 4.67 (ddd, 1 H, J = 1.5, 4.8, 5.9 Hz), 6.55 (dd, 1 H, J = 1.5, 5.9 Hz), 7.10–7.50 (m, 5 H). Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.12; H, 8.27.

Nucleophilic Reaction of the Dianion. [Ethoxy[2-[2-oxo-3-(hydroxyphenylmethyl)cyclohexyl]-2-phenylethyl]carbene]pentacarbonylchromium (10a). To a solution of diisopropylamine (35.2 μL, 0.25) in 1.0 mL of THF was added BuLi in hexane (0.23 mmol) at 0 °C. After 20 min the solution was cooled to −70 °C and transferred to a solution of **8a** (47 mg, 0.10 mmol; syn/anti = >97:3) in 1.5 mL of THF at −70 °C. After 30 min, a solution of benzaldehyde (15.8 mL, 0.56 mmol) in 0.1 mL of THF was added, and after additional 15 min stirring, 4 N HCl (~100 μL) was added. Then the mixture was warmed to room temperature and dried over $MgSO_4$. Solvent was removed, and the residue was purified on silica gel (10% AcOEt in hexane) to obtain 34.1 mg of the title compound (59%) as a pale yellow semisolid. The threo stereochemistry of the aldol reaction was assigned by the ^1H NMR analysis of the corresponding (propylamino)carbene complex ($PrNH_2$-treatment of **10a**), which showed a 9.3-Hz coupling between the two methynes protons, COC*H*C*H*OH: IR (CCl_4) 3620, 3560, 2945, 2865, 2060, 1870, 1702, 1458, 1375, 1260, 705, 670, 660; ^1H NMR (200 MHz, $CDCl_3$) 7.08–7.43 (m, 10 H), 4.86–5.00 (m, 3 H for a proton next to the carbene carbon, the methyne connected to the phenyl group, and the aldol methyne), 4.02 (dd, J = 10.9, 15.8 Hz, 1 H next to the carbene carbon), 3.62 (ddd, J = 3.8, 10.9, 11.4 Hz, 1 H), 3.31 (dd, J = 3.8, 15.8 Hz, 1 H), 2.66–2.89 (m, 2 H), 1.4–1.7 (m, 6 H), 1.43 (t, J = 7.1 Hz, 3 H). Anal. Calcd for $C_{29}H_{28}O_8Cr$: C, 62.59; H, 5.07. Found: C, 62.40; H, 5.23.

[Ethoxy[2-[2-oxo-3-(hydroxyphenylmethyl)-5-thiacyclohexyl]-2-phenylethyl]carbene]pentacarbonylchromium (10b). Prepared from **8b** in the same manner as described for **10a** (0.1 mmol, syn/anti = 96:4) in 37% yield (21.2 mg): IR (CCl_4) 3605, 2920, 2060, 1945, 1718, 1245, 658; ^1H NMR (500 MHz, $CDCl_3$) 7.15–7.43 (m, 10 H), 5.28 (dd, J = 3.7, 8.7 Hz, H_j), 4.88–4.96 (m, 2 H, ethoxy), 4.12 (dd, J = 11.5, 17.0 Hz, H_a), 3.92 (ddd, J = 3.7, 11.0, 11.5 Hz, H_c), 3.29 (dd, J = 3.7, 17.0 Hz, H_b), 3.07–3.15 (m, H_d and H_i), 2.86 (d, J = 3.7 Hz, H_k), 2.68 (dd, J = 3.7, 13.8 Hz, H_h), 2.61 (dd, J = 3.7, 13.7 Hz, H_g), 2.52 (dd, J = 7.8, 13.7 Hz, H_f), 2.35 (dd, J = 7.3, 13.8 Hz, H_e), 1.46 (t, J = 6.9 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) 14.8, 33.9, 34.9, 41.6, 56.4, 58.8, 66.7, 73.8, 78.1, 126.7, 127.2, 128.2, 128.6, 128.8, 128.8, 213.0, 216.1, 223.0. Anal. Calcd for $C_{28}H_{26}O_8CrS$: C, 58.53; H, 4.56. Found: C, 58.66; H, 4.75.

Coupling analysis indicated the diequatorial orientation of the two bulky groups on the thiacyclohexanone ring and the threo sterochemistry of the aldol moiety.



Careful analysis of the NMR spectra indicated the presence of ca. 10% of isomers, and capillary GC analysis of the corresponding ethyl ester (CAN oxidation) showed a major peak at a 90% area relative to a few minor isomers.

[1-Ethoxy-3-(2-oxocyclohexyl)-3-phenylpropyl]tributyltin. A mixture of **8a** (17 mg, 0.038 mmol), tributyltin hydride (30.5 μL, 0.113 mmol), and pyridine (~30 μL, 0.4 mmol) in 1.5 mL of hexane was heated at 70 °C for 14 h. Solvent was removed, and the residue was purified on silica gel (10% AcOEt in hexane) to give 16.3 mg of the title compound (76%). Although the product showed a single peak on capillary GC analysis (HR-1, 250 °C, 11.3 min), its ^1H NMR data indicated that it consists of a nearly 1:1 mixture of stereoisomers: IR (neat) 2955, 2930, 2855, 1938, 1715, 1455, 1130, 1085, 705; ^1H NMR (200 MHz, $CDCl_3$) 7.1–7.35 (m, 5 H), 3.35–3.65 (m, 2 H), 2.9–3.2 (m, 1 H), 2.15–2.65 (m, 4 H), 1.15–1.9 (m, 29 H), 0.7–0.95 (m, 9 H); MS (m/z, relative intensity) EI 550 (M^+, 2), 493 (6), 291 (11), 259 (9), 234 (19), 177 (26), 161 (100).

The Oxygen Anion Approach. [Ethoxy[2-[4-(1-hydroxy-2-methylpropyl)thienyl]]carbene]pentacarbonyltungsten. To a solution of thiophene (202 mg, 2.4 mmol) in 5 mL of THF was added a solution of 1.58 M BuLi in hexane (1.4 mL, 2.2 mmol) at 0 °C. After 1 h, the mixture was transferred into a suspension of tungsten hexacarbonyl (704 mg, 2.0 mmol) in 5 mL of THF at 0 °C. After 1 h the mixture was cooled to −70 °C, and LDA in THF (prepared from diisopropylamine (306 mg, 3.0 mmol) and 1.58 BuLi in hexane (1.9 mL, 3.0 mmol)) was added. After 1 h, 2-methylpropanal (216 mg, 3.0 mmol) was added. After stirring for 1 h, 90 μL of H_2O was added. After warming to room temperature, solvent was removed, and 5 mL of CH_2Cl_2 and 5 mL of H_2O were added to the residue. A ca. 1 M solution of Et_3OBF_4 in CH_2Cl_2 was added until the pH of the aqueous layer became 5. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with brine and dried with $MgSO_4$. Solvent was removed and the residue was purified on silica

gel (15% AcOEt in hexane) to obtain 952 mg of the title compound (89%): IR ($CHCl_3$) 2030, 1935, 1435, 595; ^1H NMR (200 MHz, $CDCl_3$) 8.04 (d, J = 4.2 Hz, 1 H), 7.04 (d, J = 4.2 Hz, 1 H), 4.96 (q, J = 6.7 Hz, 2 H), 4.60 (d, J = 5.7 Hz, 1 H), 2.47 (br s, 1 H), 1.8–2.1 (m, 1 H), 1.63 (t, J = 6.7 Hz, 3 H), 1.00 (d, J = 6.7 Hz, 3 H), 0.93 (d, J = 6.7 Hz, 3 H). Anal. Calcd for $C_{16}H_{16}O_7SW$: C, 35.84; H, 3.01. Found: C, 36.08; H, 3.04.

Physical Properties of the Heteroaromatic Carbene Complexes. [Ethoxy[2-[4-(1-hydroxy-2-methylpropyl)furyl]]carbene]pentacarbonyltungsten. Prepared from furan (163 mg, 2.4 mmol), $W(CO)_6$ (704 mg, 2.0 mmol), and isobutyraldehyde (216 mg, 3.0 mmol) in 79% yield (818 mg): IR ($CHCl_3$) 2030, 1930, 1485, 1190, 1015, 900, 595; ^1H NMR (200 MHz, $CDCl_3$) 7.06 (d, J = 3.8 Hz, 1 H), 6.50 (d, J = 3.8 Hz, 1 H), 4.92 (q, J = 6.7 Hz, 2 H), 4.44 (m, 1 H), 2.40 (m, 1 H), 2.24 (dqq, J = 6.7, 6.7, 6.7 Hz, 1 H), 1.40 (t, J = 6.7 Hz, 3 H), 1.00 (t, J = 6.7 Hz, 3 H), 0.91 (d, J = 6.7 Hz, 3 H). Anal. Calcd for $C_{16}H_{16}O_8W$: C, 36.95; H, 3.10. Found: C, 36.70; H, 3.01.

[Ethoxy[2-[4-(1-hydroxycyclohexyl)furyl]]carbene]pentacarbonyltungsten. Prepared from furan (82 mg, 1.2 mmol), $W(CO)_6$ (352 mg, 1.0 mmol), and cyclohexanone (147 mg, 1.5 mmol) in 27% yield (296 mg): IR ($CHCl_3$) 2030, 1935, 1490, 590; ^1H NMR (200 MHz, $CDCl_3$) 7.04 (d, J = 3.7 Hz, 1 H), 6.50 (d, J = 3.7 Hz, 1 H), 4.96 (q, J = 6.9 Hz, 2 H), 1.62 (t, J = 6.9 Hz, 3 H), 1.5–2.2 (m, 10 H). Anal. Calcd for $C_{18}H_{18}O_8W$: C, 39.58; H, 3.32. Found: C, 39.85; H, 3.56.

[Ethoxy[2-[4-(1-hydroxyphenylmethyl)thienyl]]carbene]pentacarbonyltungsten. Prepared from thiophene (20.2 mg, 0.24 mmol), $W(CO)_6$ (70.4 mg, 0.20 mmol), and benzaldehyde (31.8 mg, 0.30 mmol) in 61% yield (59.5 mg): IR ($CHCl_3$) 2030, 1935, 1440, 1195, 595; ^1H NMR (200 MHz, $CDCl_3$) 8.03 (d, J = 4.2 Hz, 1 H), 7.2–7.3 (m, 5 H), 6.97 (dd, J = 1.0, 4.2 Hz, 1 H), 5.94 (s, 1 H), 4.94 (q, J = 7.0 Hz, 2 H), 2.34 (br s, 1 H), 1.61 (t, J = 7.0 Hz, 3 H). Anal. Calcd for $C_{19}H_{14}O_7SW$: C, 40.02; H, 2.47. Found: C, 40.23; H, 2.20.

[Ethoxy[2-[4-[1-hydroxy-2-(benzyloxy)-2-cyclohexylethyl]thienyl]]carbene]pentacarbonyltungsten. Prepared from thiophene (202 mg, 2.4 mmol), $W(CO)_6$ (704 mg, 2.0 mmol), and (benzyloxy)cyclohexylacetaldehyde (697 mg, 3.0 mmol) in 65% yield (899 mg). ^1H NMR analysis indicated that the product is a 1:1 mixture of stereoisomers, which could not be separated on TLC (AcOEt/hexane): IR (CCl_4), 2920, 2030, 1935, 1195; ^1H NMR (200 MHz, $CDCl_3$) 8.07 (d, J = 4.2 Hz, 0.5 H), 8.04 (d, J = 4.1 Hz, 0.5 H), 7.1–7.4 (m, 5 H), 7.12 (d, J = 4.1 Hz, 0.5 H), 7.10 (d, J = 4.2 Hz, 0.5 H), 4.8–5.1 (m, 2 H), 4.66 (d, J = 11.0 Hz, 0.5 H), 4.56 (d, J = 10.8 Hz, 0.5 H), 4.50 (d, J = 11.0 Hz, 0.5 H), 4.33 (d, J = 10.8 Hz, 0.5 H), 3.41 (m, 1 H), 3.20 (br s, 0.5 H), 2.46 (br s, 0.5 H), 1.65 (t, J = 7.1 Hz, 1.5 H), 1.64 (t, J = 7.1 Hz, 1.5 H), 1.4–2.0 (m, 5 H), 1.0–1.4 (m, 6 H). Anal. Calcd for $C_{27}H_{28}O_8SW$: C, 46.57; H, 4.05. Found: C, 46.27; H, 4.15.

[Ethoxy[2-[4-(4,4-dimethyl-2-oxa-3-oxocyclopentyl)thienyl]]carbene]pentacarbonyltungsten. Prepared from thiophene (84 mg, 1.0 mmol), $W(CO)_6$ (370 mg, 1.05 mmol), and ethyl 2,2-dimethyl-4-oxobutanoate (190 mg, 1.2 mmol) in 48% yield (274 mg). In this preparation, the solution of the carbene dianion was added via a canula to a cooled (−78 °C) solution of the aldehyde in THF. Lactonization took place spontaneously during the biphasic ethylation stage: IR (CCl_4) 2035, 1945, 1790, 1225, 1190; ^1H NMR (270 MHz, $CDCl_3$) 8.06 (d, J = 4.2 Hz, 1 H), 7.17 (dd, J = 1.0, 4.2 Hz, 1 H), 5.58 (dd, J = 6.8, 9.4 Hz, 1 H), 4.99 (q, J = 7.0 Hz, 2 H), 2.58 (dd, J = 6.8, 13.4 Hz, 1 H), 2.20 (dd, J = 9.4, 13.4 Hz, 1 H), 1.65 (t, J = 7.0 Hz, 3 H), 1.36 (s, 3 H), 1.32 (s, 3 H). Anal. Calcd for $C_{18}H_{16}O_8SW$: C, 37.52; H, 2.79. Found: C, 37.91; H, 2.99.

[Etboxy[2-[4-(etboxycarbonyl)thienyl]]carbene]pentacarbonyltungsten. Prepared from thiophene (202 mg, 2.4 mmol) $W(CO)_6$ (704 mg, 2.0 mmol), and ethyl chloroformate (326 mg, 3.0 mmol) in 60% yield (645 mg): IR (CCl_4) 2030, 1945, 1715, 1245, 1175; ^1H NMR (200 MHz, $CDCl_3$) 8.02 (d, J = 4.4 Hz, 1 H), 7.78 (d, J = 4.4 Hz, 1 H), 5.01 (q, J = 7.1 Hz, 2 H), 4.39 (q, J = 7.1 Hz, 2 H), 1.69 (t, J = 7.1 Hz, 3 H), 1.40 (t, J = 7.1 Hz, 3 H). Anal. Calcd for $C_{15}H_{12}O_8SW$: C, 33.60; H, 2.26. Found: C, 33.80; H, 2.18.

[Ethoxy[2-[4-(trimethylsilyl)thienyl]]carbene]pentacarbonyltungsten (15d). Prepared from thiophene (101 mg, 1.2 mmol), $W(CO)_6$ (352 mg, 1.0 mmol), and Me_3SiCl (304 mg, 2.8 mmol) in 63% yield (337 mg): IR (CCl_4) 2030, 1975, 1940, 1215, 1205, 1190, 1065, 990, 845; ^1H NMR (200 MHz, $CDCl_3$) 8.20 (d, J = 3.8 Hz, 1 H), 7.31 (d, J = 3.8 Hz, 1 H), 4.97 (q, J = 7.0 Hz, 2 H), 1.69 (t, J = 7.0 Hz, 3 H), 0.36 (s, 9 H). Anal. Calcd for $C_{15}H_{16}O_6SSiW$: C, 33.60; H, 3.01. Found: C, 33.88; H, 2.99.

[Ethoxy[2-[4-(hydroxyphenylmethyl)furyl]]carbene]pentacarbonylchromium. Prepared from furan (163 mg, 2.4 mmol), $Cr(CO)_6$ (440 mg, 2.0 mmol), and benzaldehyde (318 mg, 3.0 mmol) in 69% yield (583 mg): IR ($CHCl_3$) 2025, 1940, 1485, 1015, 895, 645; ^1H NMR (200 MHz, $CDCl_3$) 8.11 (d, J = 4.6 Hz, 1 H), 7.2–7.5 (m, 5 H), 7.00 (d, J = 4.6 Hz, 1 H), 5.98 (d, J = 3.4 Hz, 1 H), 4.13 (q, J = 7.2 Hz, 2 H), 2.67 (d, J = 3.4 Hz, 1 H), 1.63 (t, J = 7.2 Hz, 3 H). Anal. Calcd for $C_{19}H_{14}O_8Cr$: C, 54.04; H, 3.34. Found: C, 53.80; H, 3.19.

[Ethoxy[2-[4-(hydroxyphenylmethyl)thienyl]]carbene]pentacarbonylchromium. Prepared from thiophene (20.2 mg, 0.24 mmol), $Cr(CO)_6$ (44 mg, 0.20 mmol), and benzaldehyde (31.8 mg, 0.30 mmol) in 62% yield (54 mg): IR ($CHCl_3$) 2025, 1940, 1440, 1190, 685, 665, 645; ^1H NMR (200 MHz, $CDCl_3$) 8.11 (d, J = 4.2 Hz, 1 H), 7.2–7.6 (m, 5 H), 7.00 (d, J = 4.2 Hz, 1 H), 5.97 (d, J = 2.9 Hz, 1 H), 5.11 (q, J = 6.7 Hz, 2 H), 2.77 (br s, 1 H), 1.60 (t, J = 6.7 Hz, 3 H). Anal. Calcd for $C_{19}H_{14}O_7SCr$: C, 52.06; 3.22. Found: C, 52.36; 3.50.

[Ethoxy[2-[4-(1-hydroxy-2-methylpropyl)thienyl]]carbene]pentacarbonylchromium. Prepared from thiophene (202 mg, 2.4 mmol), $Cr(CO)_6$ (440 mg, 2.0 mmol), and isobutyraldehyde (216 mg, 3.0 mmol) in 64% yield (515 mg): IR ($CHCl_3$) 2020, 1935, 1440, 1190, 1160, 680, 665, 645; ^1H NMR (200 MHz, $CDCl_3$) 8.14 (br s, 1 H), 7.04 (br s, 1 H), 5.13 (q, J = 7.4 Hz, 2 H), 4.63 (m, 1 H), 2.37 (m, 1 H), 2.00 (m, 1 H), 1.64 (t, J = 7.4 Hz, 3 H), 0.7–1.1 (m, 6 H). Anal. Calcd for $C_{16}H_{16}O_7SCr$: C, 47.53; H, 3.99. Found: C, 47.80; H, 3.82.

[Ethoxy[2-[4-(1-hydroxy-2-phenylpropyl)thienyl]]carbene]pentacarbonyltungsten. Prepared from thiophene (101 mg, 1.2 mmol), $Cr(CO)_6$ (220 mg, 1.0 mmol), and 2-phenylpropionaldehyde (201 mg, 1.5 mmol) in 87% yield (407 mg): IR (CCl_4) 2025, 1980, 1945, 1195, 680, 665; ^1H NMR (200 MHz, $CDCl_3$) 8.04 (d, J = 3.8 Hz, 1 H), 7.20 (m, 5 H), 6.79 (d, J = 3.8 Hz, 1 H), 5.11 (q, J = 6.7 Hz, 2 H), 4.99 (m, 1 H), 3.14 (dq, J = 6.8, 6.8 Hz, 1 H), 2.31 (br s, 1 H), 1.63 (t, J = 6.7 Hz, 3 H), 1.34 (d, J = 6.8 Hz, 3 H). Anal. Calcd for $C_{21}H_{18}O_7SCr$: C, 54.08; H, 3.89. Found: C, 54.34; H, 3.99.

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