

Synthesis, Structure, and Reactivity of Cyclic (Arene)chromium Carbene Complexes

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In contrast to benzannulation products obtained by photolysis, thermolysis of the chromium carbene complexes [(1,1'-biphenyl-2-yl)methoxymethylene]pentacarbonylchromium (1) and [(1,1'-biphenyl-2-yl)(dimethylamino)methylene]pentacarbonylchromium (4) provide the new cyclic arene carbene complexes [(1',2',3',4',5',6'- η)-1,1'-biphenyl-2-yl]methoxymethylene]dicarbonylchromium (3) and [(1',2',3',4',5',6'- η)-1,1'-biphenyl-2-yl](dimethylamino)methylene]dicarbonylchromium (5). The ¹³C NMR spectra of these new complexes have unusually high-field-shifted and low-field-shifted signals for the carbene and carbonyl carbon resonances, respectively. The complexes are remarkably stable and do not show the high electrophilic behavior typical of Fischer carbene complexes. A new protocol for the aminolysis of Fischer carbene complexes is reported. The structure of complexes 3 and 5 were determined by single-crystal X-ray diffraction studies. 3 crystallizes in the monoclinic space group C2/c with unit cell dimensions $a = 16.154$ (2) Å, $b = 12.256$ (2) Å, $c = 15.575$ (2) Å, and $\beta = 122.92$ (1)°, with $Z = 8$. 5 crystallizes in the monoclinic space group P2₁/n with unit cell dimensions $a = 11.47$ (1) Å, $b = 7.082$ (7) Å, $c = 20.87$ (2) Å, and $\beta = 108.13$ (2)°, with $Z = 4$. The structures were refined by full-matrix least-squares procedures to final $R = 0.028$ and $R_w = 0.050$ for 2074 unique observed reflections for 3 and $R = 0.066$ and $R_w = 0.101$ for 1580 unique observed reflections for 5.

Introduction

The chemistry of group VI Fischer carbene complexes has been developed to provide access to a remarkably diverse array of products and has even progressed into the realm of total synthesis endeavors.² Yet, the rapid development of new reactions and synthetic methodology continues unabated more than 25 years after their discovery by Fischer in 1964.³ Reports in the literature since 1990 have described new reactions and products, including C-H insertion reactions,⁴ ene reactions,⁵ alkoxymalonates,⁶ α -amino esters,⁷ azapentatrienes,⁸ bicyclic cyclobutanones,⁹ bicyclic lactones,¹⁰ butenolides,¹¹ dihydrobenzenes,¹² dihydropyrans,¹³ hydrazido complexes,¹⁴ nitrogen heterocycles,¹⁵ pyridines,¹⁶ pyrroles,¹⁶ α -silyl vinyl ether complexes,¹⁷

η^4 -vinylketene complexes,¹⁸ and 3-vinyl-2-oxazolidinones.¹⁹ Recently, we reported a new photochemical benzannulation reaction of dienylchromium carbene complexes that provides access to ortho-substituted aromatic alcohols, thus providing a complementary reaction to the synthetically important alkyne plus chromium carbene benzannulation reaction (Dötz reaction).²⁰ We proposed the intermediacy of photogenerated chromium-complexed dienylketenes, which undergo electrocyclization reactions, and demonstrated the rapid construction of polycyclic aromatic alcohols. In contrast to the photochemical reaction, thermal reaction of dienyl carbene complexes can proceed by entirely different pathways. We report herein on the contrasts between photochemical and thermal reactions of biphenyl carbene complexes which yield novel cyclic (arene)chromium carbene complexes.

Results

As part of our investigation into the chemistry of dienylchromium carbene complexes, we examined the reactivity of the biphenyl carbene complex 1, which was readily prepared by standard methods (eq 1). Reaction of 1 under photolysis conditions (450-W Hanovia lamp, Pyrex filtering) in THF solvent provided an excellent yield of 9-hydroxy-10-methoxyphenanthrene (2; eq 1). This is the expected benzannulation product arising from electrocyclization of a photogenerated chromium-complexed biphenylketene intermediate as we have reported.²⁰ In an

(1) Address correspondence concerning the X-ray crystallographic studies to this author.

(2) For reviews, see: (a) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1990; Vol. 5. (b) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, CT, 1989; Vol. 1. (c) *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluwer Academic Publishers: Hingham, MA, 1989. (d) Wulff, W. D.; Tang, P.-C.; Chan, K.-S.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* 1985, 41, 5813. (e) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1984. (f) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* 1984, 23, 587.

(3) Fischer, E. O.; Massböl, A. *Angew. Chem., Int. Ed. Engl.* 1964, 3, 580.

(4) Wienand, A.; Reissig, H.-U. *Angew. Chem., Int. Ed. Engl.* 1990, 29, 1129.

(5) Faron, K. L.; Wulff, W. D. *J. Am. Chem. Soc.* 1990, 112, 8615.

(6) Lee, S.; Cooper, N. J. *J. Am. Chem. Soc.* 1990, 112, 9419.

(7) Hegedus, L. S.; Schwindt, M. A.; De Lombaert, S.; Imwinkelried, R. *J. Am. Chem. Soc.* 1990, 112, 2264.

(8) Aumann, R.; Schröder, J. *Chem. Ber.* 1990, 123, 2053.

(9) Söderberg, B. C.; Hegedus, L. S.; Sierra, M. A. *J. Am. Chem. Soc.* 1990, 112, 4364.

(10) Brandvold, T. A.; Wulff, W. D. *J. Am. Chem. Soc.* 1990, 112, 1645.

(11) Hoye, T. R.; Rehberg, G. M. *J. Am. Chem. Soc.* 1990, 112, 2841.

(12) Wang, S. L. B.; Wulff, W. D. *J. Am. Chem. Soc.* 1990, 112, 4550.

(13) Söderberg, B. C.; Hegedus, L. S. *Organometallics* 1990, 9, 3113.

(14) Sleiman, H. F.; Arndtsen, B. A.; McElwee-White, L. *Organometallics* 1991, 10, 541.

(15) (a) Dötz, K. H.; Schäfer, T.; Harms, K. *Angew. Chem., Int. Ed. Engl.* 1990, 29, 176. (b) Audouin, M.; Blandinieres, S.; Parlier, A.; Rudler, H. *J. Chem. Soc., Chem. Commun.* 1990, 23.

(16) (a) Dragsich, V.; Murray, C. K.; Warner, B. P.; Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* 1990, 112, 1251. (b) Dragsich, V.; Wulff, W. D.; Hoogsteen, K. *Organometallics* 1990, 9, 2867. (c) Denise, B.; Goumont, R.; Parlier, A.; Rudler, H.; Daran, J. C.; Vaissermann, J. *J. Chem. Soc., Chem. Commun.* 1990, 1238. (d) Aumann, R.; Heinen, H.; Krüger, C.; Betz, P. *Chem. Ber.* 1990, 123, 599.

(17) Macomber, D. W.; Madhukar, P.; Rogers, R. D. *Organometallics* 1991, 10, 2121.

(18) Anderson, B. A.; Wulff, W. D. *J. Am. Chem. Soc.* 1990, 112, 1645.

(19) Montgomery, J.; Wieber, G. M.; Hegedus, L. S. *J. Am. Chem. Soc.* 1990, 112, 6255.

(20) Merlic, C. A.; Xu, D. *J. Am. Chem. Soc.* 1991, 113, 7418.

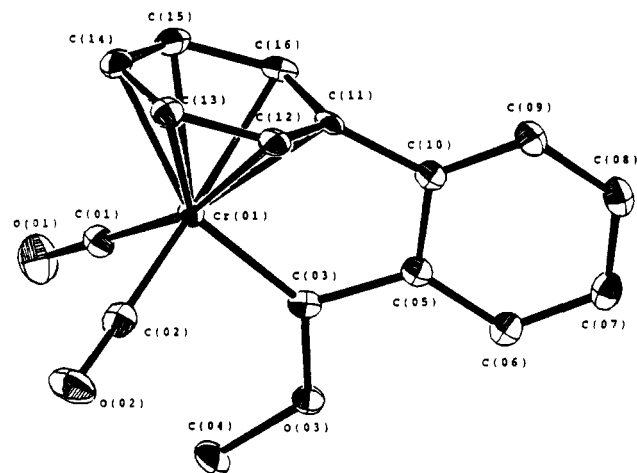
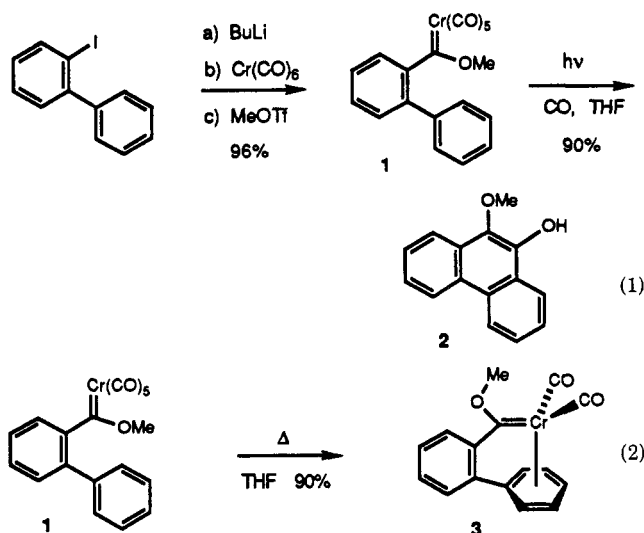


Figure 1. ORTEP plot of the arene carbene complex 3.

attempt to determine if thermal reaction of carbene 1 would also generate the benzannulation product 2, we reacted 1 in refluxing THF for 36 h. The initially orange solution turned dark within 12 h, and continued heating did not result in any change in TLC behavior, nor, in particular, was there any trace of the desired product 2. Instead, a black crystalline material was obtained. The infrared spectrum contained strong absorptions at 1926 and 1870 cm^{-1} . The ^1H NMR spectrum of the product contained signals at 5.40, 5.46, and 5.66 ppm, while the ^{13}C NMR spectrum contained signals from 94 to 115 ppm and at 321 ppm. Altogether, these data suggested the presence of the chromium arene carbene complex 3 as illustrated in eq 2.

This proposal was confirmed by an X-ray crystallographic study, and the resulting structure is illustrated in Figure 1. The structure is highly symmetric with a pseudooctahedral geometry about the chromium center and the methoxy group bisecting the OC-Cr-CO angle. The chromium to carbene carbon bond length of 1.953 Å is short for a chromium carbene complex but is very close to that observed (1.932 Å) in the analogous arene carbene complex $(\text{PhH})\text{Cr}(\text{CO})_2\text{C}(\text{OMe})\text{Ph}$ prepared by Fischer and co-workers²¹ and structurally characterized by Schubert.²² The planes of the two aryl rings are nearly perpendicular with a dihedral angle of 82°, while the planes of the carbene moiety (defined by Cr-C(03)-C(06)) and the bridging aryl ring are essentially coplanar with a dihedral angle of 3° between them. Ring strain slightly distorts complexation of chromium to the arene ring away from the ring centroid such that the Cr-C(11) bond (2.166 Å) is shorter than the Cr-C(14) bond (2.260 Å). These bond lengths are on the short and long ends of the normal range seen for chromium arene complexes.²³ Further details (atomic coordinates, bond lengths, and bond angles) of the structure are provided in Tables I and II.

Concerning reactivity, complex 3 is remarkably unreactive for a Fischer carbene and an (arene)chromium complex. It is air-stable and does not exhibit the high electrophilic behavior at the carbene carbon typical of Fischer carbene complexes. For example, reaction of 3 with phenyllithium in THF at -78°C results in *complete recovery of the starting complex*, while reaction at room temperature for 20 h results in 70% recovery. No evidence

Table I. Atomic Coordinates and Equivalent Isotropic Temperature Factors for Complex 3

atom	x	y	z	$10^4 U_{\text{eq}}^a, \text{Å}^2$
Cr(01)	0.9745 (1)	0.2239 (1)	0.0089 (1)	116 (4)
O(01)	1.1075 (1)	0.1962 (1)	-0.0682 (1)	307 (18)
O(02)	0.9219 (1)	0.4316 (1)	-0.1116 (1)	296 (17)
O(03)	0.8217 (1)	0.1271 (1)	-0.1999 (1)	174 (13)
C(01)	1.0558 (2)	0.2038 (2)	-0.0391 (2)	171 (20)
C(02)	0.9404 (2)	0.3512 (2)	-0.0655 (2)	186 (19)
C(03)	0.8624 (2)	0.1408 (2)	-0.0983 (2)	137 (17)
C(04)	0.8601 (2)	0.1853 (2)	-0.2514 (2)	251 (22)
C(05)	0.8007 (2)	0.0752 (2)	-0.0723 (2)	140 (18)
C(06)	0.7176 (2)	0.0128 (2)	-0.1408 (2)	171 (19)
C(07)	0.6650 (2)	-0.0405 (2)	-0.1064 (2)	197 (19)
C(08)	0.6918 (2)	-0.0310 (2)	-0.0053 (2)	204 (21)
C(09)	0.7747 (2)	0.0303 (2)	0.0640 (2)	183 (19)
C(10)	0.8286 (2)	0.0814 (2)	0.0303 (2)	144 (18)
C(11)	0.9204 (2)	0.1457 (2)	0.0939 (2)	134 (17)
C(12)	0.9159 (2)	0.2593 (2)	0.1056 (2)	150 (18)
C(13)	1.0024 (2)	0.3226 (2)	0.1436 (2)	169 (19)
C(14)	1.0917 (2)	0.2737 (2)	0.1704 (2)	182 (20)
C(15)	1.0959 (2)	0.1597 (2)	0.1603 (2)	186 (19)
C(16)	1.0113 (2)	0.0951 (2)	0.1239 (2)	165 (18)

$$^a U_{\text{eq}} = [1/(6\pi^2)] \sum \sum \beta_{ij} a_i a_j$$

Table II. Selected Bond Lengths and Bond Angles for Complex 3

(a) Bond Lengths (Å)			
Cr(01)-C(01)	1.847 (2)	Cr(03)-C(05)	1.498 (3)
Cr(01)-C(02)	1.840 (2)	C(05)-C(06)	1.403 (3)
Cr(01)-C(03)	1.954 (2)	C(05)-C(10)	1.407 (3)
Cr(01)-C(11)	2.166 (2)	C(06)-C(07)	1.389 (3)
Cr(01)-C(16)	2.213 (2)	C(07)-C(08)	1.393 (3)
Cr(01)-C(12)	2.214 (2)	C(08)-C(09)	1.397 (3)
Cr(01)-C(15)	2.236 (2)	C(09)-C(10)	1.387 (3)
Cr(01)-C(13)	2.245 (2)	C(10)-C(11)	1.485 (3)
Cr(01)-C(14)	2.260 (2)	C(11)-C(12)	1.411 (3)
O(01)-C(01)	1.150 (3)	C(11)-C(16)	1.419 (3)
O(02)-C(02)	1.159 (3)	C(12)-C(13)	1.416 (3)
O(03)-C(03)	1.354 (3)	C(14)-C(15)	1.412 (3)
O(03)-C(04)	1.441 (3)	C(15)-C(16)	1.405 (2)
(b) Bond Angles (deg)			
O(01)-C(01)-Cr(01)	176.91 (20)	C(05)-C(03)-Cr(01)	119.52 (15)
O(02)-C(02)-Cr(01)	177.88 (20)	C(06)-C(05)-C(03)	126.12 (19)
O(03)-C(03)-Cr(01)	134.35 (15)	C(10)-C(05)-C(03)	115.39 (18)
C(02)-Cr(01)-C(01)	83.89 (10)	C(09)-C(10)-C(11)	126.31 (20)
C(01)-Cr(01)-C(03)	96.73 (9)	C(05)-C(10)-C(11)	111.94 (18)
C(02)-Cr(01)-C(03)	94.78 (9)	C(12)-C(11)-C(10)	120.46 (18)
C(03)-O(03)-C(04)	120.43 (16)	C(16)-C(11)-C(10)	117.86 (18)
O(03)-C(03)-C(05)	106.12 (17)	C(10)-C(11)-Cr(01)	114.55 (14)

of nucleophilic attack at the carbene carbon or the arene ring was obtained. Realizing that the arene might be deprotonated²⁴ or undergo nucleophilic addition²⁵ under

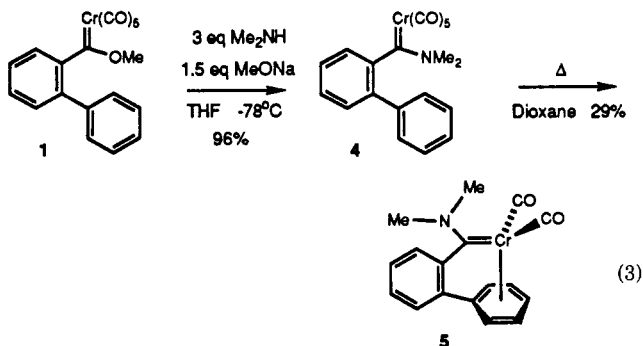
(21) Fischer, E. O.; Stücker, P.; Beck, H.-J.; Kreissl, F. R. *Chem. Ber.* 1976, 109, 3089.

(22) Schubert, U. J. *Organomet. Chem.* 1980, 185, 373.

(23) Mills, O. S. *Pure Appl. Chem.* 1969, 20, 117.

these conditions, we also treated **3** with *tert*-butyllithium followed by D₂O or methyl triflate. Neither experiment indicated any reaction of complex **3**. This level of resistance to nucleophilic attack and deprotonation is unprecedented in the chemistry of Fischer carbene complexes² and (arene)chromium complexes.²⁶

Next we turned to aminolysis, but finding **3** inert to standard conditions,²⁷ the method developed by Fischer involving carbyne intermediates was attempted.²¹ However, treatment of complex **3** with boron trichloride followed by dimethylamine resulted in extensive decomposition. Presumably, the expected intermediate cationic carbyne complex is not stable under the reaction conditions due to ring strain. A successful alternative route to the amino arene carbene complex involved aminolysis of **1** first, then thermolysis (eq 3). Direct aminolysis of Fischer



carbene complexes with monosubstituted amines is generally quite efficient, but problems are encountered with disubstituted amines.^{27a} Indeed, direct aminolysis of **1** with excess dimethylamine under various conditions provided, at best, 25% of the aminocarbene complex. Recognizing from the work of Fischer on the mechanism of aminolysis that the reaction rate depends on the concentration of a proton acceptor in addition to that of the amine,²⁸ we found that the presence of sodium methoxide greatly enhanced the rate of aminolysis of carbene complex **1** and is particularly useful for aminolyses in general when employing disubstituted amines as in eq 3.²⁹ Aminolysis of complex **1** with excess dimethylamine in the presence of catalytic amounts of sodium methoxide raised the yields

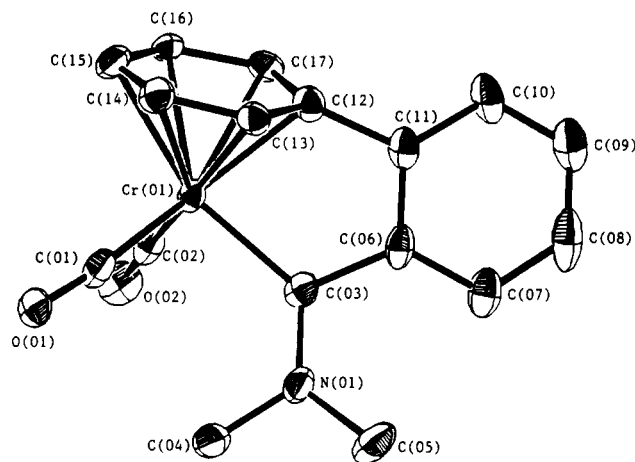


Figure 2. ORTEP plot of the arene carbene complex **5**.

to 75%, and use of 1.5 equiv of sodium methoxide in THF at -78°C for 20 min resulted in a 96% yield of the (dimethylamino)carbene complex **4**. Thus, this method provides a dramatic improvement over the direct aminolysis.

Thermolysis of aminocarbene **4** was quite sensitive to reaction conditions (eq 3). Under optimized conditions, **4** was gently refluxed in dioxane solvent with nitrogen sparging for 52 h and the product isolated by silica gel chromatography at -40°C to provide complex **5** in 29% yield. The isolated product was quite stable yet decomposed under standard chromatography conditions. We speculated that the dimethylamino group might be twisted out of the molecular plane due to steric interactions with the adjacent aryl hydrogen, thus reducing its interaction with the carbene carbon and enhancing its basicity. This was borne out in the X-ray crystal structure (vide infra).

The ¹H and ¹³C NMR spectra of complex **5** were unusual in that the resonances for the methyl groups, but no other signals, were unusually broad. The methyl signals in the ¹H spectrum were at 3.49 and 3.64 ppm and had peak widths at half-height of 40 Hz. The ¹³C NMR signals at 47.9 and 52.2 ppm were very broad signals that were only observable in spectra with high signal to noise ratios. Since the corresponding signals in complex **4** were quite sharp, this indicated that there was more rapid exchange of the methyl groups and that the barrier to rotation³⁰ about the carbene carbon to nitrogen bond was significantly less in **5**. We again speculated that the dimethylamino group might be twisted away from optimal conjugation with the carbene carbon due to steric interactions with the adjacent aryl hydrogen and that this raised the ground-state energy such that the activation energy for rotation of the dimethylamino group in **5** is reduced compared to that in complex **4**.

The proposed structure was confirmed by an X-ray crystal analysis, and the structure found is illustrated in Figure 2. The structure has a pseudooctahedral geometry about the chromium center but is distorted due to steric interactions between the dimethylamino group and the adjacent aryl ring. The chromium to carbene carbon bond length (2.047 Å) is short for an amino chromium carbene complex.³¹ The planes of the two aryl rings are nearly perpendicular with a dihedral angle of 98° between them.

(30) (a) Kreiter, C. G.; Fischer, E. O. In *XXIII International Congress of Pure and Applied Chemistry*; Butterworths: New York, 1971; Vol. 6, pp 151-168. (b) Kreiter, C. G.; Fischer, E. O. *Angew. Chem., Int. Ed. Engl.* 1969, 8, 761.

(31) Schubert, U. In *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1984.

(24) For examples, see: (a) Semmelhack, M. F.; Bisaha, J.; Czarny, M. *J. Am. Chem. Soc.* 1979, 101, 768. (b) Card, R. J.; Trahanovsky, W. S. *J. Org. Chem.* 1980, 45, 2555, 2560. (c) Ghavshou, M.; Widdowson, D. A. *J. Chem. Soc., Perkin Trans. 1* 1983, 3065. (d) Fukui, M.; Ikeda, T.; Oishi, T. *Chem. Pharm. Bull.* 1983, 31, 466.

(25) (a) Semmelhack, M. F.; Seufert, W.; Keller, L. *J. Am. Chem. Soc.* 1980, 102, 6584. (b) Semmelhack, M. F.; Yamashita, A. *J. Am. Chem. Soc.* 1980, 102, 5924. (c) Semmelhack, M. F.; Clark, G. R.; Garcia, J. L.; Harrison, J. J.; Thebtaranonth, Y.; Wulff, W.; Yamashita, A. *Tetrahedron* 1981, 37, 3957. (d) Semmelhack, M. F.; Zask, A. *J. Am. Chem. Soc.* 1983, 105, 2034. (e) Semmelhack, M. F.; Garcia, J. L.; Cortes, G. D.; Farina, R.; Hong, R.; Carpenter, B. K. *Organometallics* 1983, 2, 467.

(26) For reviews of (arene)chromium complexes, see: (a) Kündig, E. P. *Pure Appl. Chem.* 1985, 57, 1855. (b) Kündig, E. P.; Do Thi, N. P.; Paglia, P.; Simmons, D. P.; Spichiger, S.; Wenger, E. In *Organometallics in Organic Synthesis*; de Meijere, A., tom Dieck, H., Eds.; Springer-Verlag: Berlin, 1987. (c) Pearson, A. J. *Metallo-Organic Chemistry*; Wiley: New York, 1985. (d) Watts, W. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: London, 1985; Vol. 3, p 1001.

(27) (a) Conner, J. A.; Fischer, E. O. *J. Chem. Soc. A* 1969, 578. (b) Fischer, E. O.; Kollmeier, H.-J. *Chem. Ber.* 1971, 104, 1339. (c) Fischer, E. O.; Heckl, B.; Werner, H. *J. Organomet. Chem.* 1971, 28, 359. (d) Fischer, E. O.; Leopold, M. *Chem. Ber.* 1972, 105, 599. (e) Fischer, E. O.; Fontana, S. *J. Organomet. Chem.* 1972, 40, 367. (f) Weiss, K.; Fischer, E. O. *Chem. Ber.* 1973, 106, 1277.

(28) Werner, H.; Fischer, E. O.; Heckl, B.; Kreiter, C. G. *J. Organomet. Chem.* 1971, 28, 367.

(29) Catalytic and stoichiometric use of sodium methoxide has been reported to promote ester aminolysis reactions. See: De Feo, R. J.; Strickler, P. D. *J. Org. Chem.* 1963, 28, 2915.

Table III. Atomic Coordinates and Equivalent Isotropic Temperature Factors for Complex 5

atom	x	y	z	$10^4 U_{eq}, \text{\AA}^2$
Cr(01)	0.4809 (1)	0.2201 (2)	0.1110 (1)	205 (10)
O(01)	0.5696 (6)	-0.1789 (9)	0.1312 (3)	331 (51)
O(02)	0.7296 (6)	0.3001 (9)	0.0974 (3)	364 (53)
N(01)	0.6072 (7)	0.2359 (10)	0.2642 (4)	264 (54)
C(01)	0.5381 (9)	-0.0220 (14)	0.1270 (4)	285 (73)
C(02)	0.6310 (9)	0.2736 (12)	0.1016 (4)	210 (64)
C(03)	0.5283 (8)	0.3134 (12)	0.2086 (4)	245 (66)
C(04)	0.6977 (9)	0.0925 (13)	0.2604 (5)	295 (69)
C(05)	0.6038 (10)	0.2542 (14)	0.3350 (5)	389 (78)
C(06)	0.4582 (9)	0.4830 (12)	0.2208 (4)	252 (71)
C(07)	0.4966 (9)	0.6153 (13)	0.2739 (5)	328 (77)
C(08)	0.4217 (11)	0.7683 (13)	0.2751 (6)	419 (92)
C(09)	0.3117 (11)	0.7969 (14)	0.2272 (5)	368 (85)
C(10)	0.2755 (9)	0.6740 (12)	0.1732 (5)	338 (81)
C(11)	0.3485 (9)	0.5210 (12)	0.1697 (5)	248 (70)
C(12)	0.3281 (8)	0.3974 (12)	0.1101 (4)	246 (67)
C(13)	0.2951 (8)	0.2052 (13)	0.1135 (4)	241 (64)
C(14)	0.3032 (9)	0.0779 (12)	0.0635 (5)	285 (71)
C(15)	0.3480 (9)	0.1365 (13)	0.0114 (5)	287 (70)
C(16)	0.3804 (8)	0.3266 (12)	0.0078 (4)	237 (66)
C(17)	0.3687 (8)	0.4587 (12)	0.0564 (4)	250 (67)

$$U_{eq} = [1/(6\pi^2)] \sum \beta_{ij} a_i a_j$$

However, the distortions about the carbene moiety are more severe. The planes of the carbene group (defined by Cr-C(03)-C(06)) and the bridging aryl ring are twisted by a dihedral angle of 21° , while the planes of the carbene group and the dimethylamino group are twisted by a dihedral angle of -20° . Ring strain again slightly distorts complexation of chromium to the arene ring such that the Cr-C(12) bond (2.151 Å) is shorter than the Cr-C(15) bond (2.241 Å). The structural twists also laterally distort complexation of the aryl ring, resulting in chromium to C(13) and C(17) bond distances of 2.150 and 2.213 Å, respectively. Such a combination of displacements is unusual for (arene)chromium complexes.^{23,26d} Further details (atomic coordinates, bond lengths, and bond angles) of the structure are provided in Tables III and IV.

Discussion

An interesting aspect of these results is the dramatic dichotomy between photochemical and thermal reactions of the carbene complexes 1 and 4. The traditional view has been that photolysis of Fischer carbene complexes induces CO loss as the primary photochemical process.³² However, as has been well demonstrated by the recent work of Hegedus, photolysis of chromium carbene complexes induces CO insertion to provide chromium-complexed ketenes which undergo further reactions such as trapping with alcohols, alkenes, and imines.³³ In the case of complex 1, photolysis generates an intermediate arylketene which cyclizes in a pericyclic reaction and the resultant dieny ketone tautomerizes to afford the phenanthrol product 2.²⁰ Nevertheless, some photoinduced CO loss must occur, since performing the reaction in the presence of CO greatly enhances the yields of benzannulated product. We have found that optimal yields of 2 are obtained using Pyrex filtering of the medium-pressure mercury lamp, while Vycor or quartz filters provide diminished yields. Photodissociation of CO likely domi-

Table IV. Bond Lengths and Bond Angles for Complex 5

(a) Bond Lengths (Å)			
Cr(01)-C(01)	1.829 (10)	C(03)-C(06)	1.510 (12)
Cr(01)-C(02)	1.831 (9)	C(06)-C(07)	1.413 (12)
Cr(01)-C(03)	2.047 (9)	C(06)-C(11)	1.399 (13)
Cr(01)-C(12)	2.151 (9)	C(07)-C(08)	1.388 (14)
Cr(01)-C(13)	2.150 (9)	C(08)-C(09)	1.359 (15)
Cr(01)-C(14)	2.212 (10)	C(09)-C(10)	1.382 (14)
Cr(01)-C(15)	2.241 (9)	C(10)-C(11)	1.385 (12)
Cr(01)-C(16)	2.234 (9)	C(11)-C(12)	1.479 (12)
Cr(01)-C(17)	2.213 (9)	C(12)-C(13)	1.421 (12)
O(01)-C(01)	1.163 (11)	C(12)-C(17)	1.409 (12)
O(02)-C(02)	1.176 (10)	C(13)-C(14)	1.404 (13)
N(01)-C(03)	1.346 (11)	C(14)-C(15)	1.402 (13)
N(01)-C(04)	1.472 (12)	C(15)-C(16)	1.405 (12)
N(01)-C(05)	1.496 (11)	C(16)-C(17)	1.417 (12)
(b) Bond Angles (deg)			
O(01)-C(01)-Cr(01)	174.01 (81)	C(03)-C(05)-Cr(05)	126.79 (77)
O(02)-C(02)-Cr(01)	176.69 (75)	C(04)-N(01)-C(05)	110.40 (72)
N(01)-C(03)-Cr(01)	128.68 (64)	N(01)-C(03)-C(06)	115.41 (76)
C(06)-C(03)-Cr(01)	115.72 (61)	C(11)-C(06)-C(03)	115.08 (76)
C(11)-C(12)-Cr(01)	115.03 (63)	C(07)-C(06)-C(03)	127.40 (87)
C(01)-Cr(01)-C(02)	85.30 (41)	C(10)-C(11)-C(12)	124.58 (89)
C(01)-Cr(01)-C(03)	98.74 (37)	C(06)-C(11)-C(12)	113.37 (77)
C(02)-Cr(01)-C(03)	94.16 (36)	C(13)-C(12)-C(11)	120.01 (77)
C(03)-N(01)-C(04)	122.06 (74)		

ates at the short wavelengths which promote d-d transitions.³⁴

In contrast with this chemistry are the thermal reactions of complexes 1 and 4. The principal thermal reaction of Fischer carbene complexes is dissociation of CO.³⁵ In complexes 1 and 4 this must be followed by η^2 -coordination of the β -aryl substituent with subsequent dissociation of two more CO ligands and ring slippage to form the η^6 -arene complex. The modest yield of arene carbene 5 may arise from inhibition of the initial coordination of the arene ring due to the steric interactions this would induce between the dimethylamino moiety and the adjacent aryl ring. These CO dissociations and arene coordinations are even evidenced in the mass spectra of 1 and 4. While the mass spectra of most Fischer carbene complexes are characterized by successive CO losses and the bare metal carbene as the base peak, compounds 1 and 4 have very intense M - 3CO signals and only weak signals for the M - CO and M - 2CO signals. At low ionization energy (16 eV), the M - 3CO signal from complex 1 is 92% of the base peak (M - 5CO) and the M - CO, M - 2CO, and M - 4CO signals are not observed. While numerous examples exist of CO substitution and inter- or intramolecular coordination of a single two-electron-donor ligand in group VI Fischer carbene complexes,³⁶ this pathway is the first example involving multiple CO substitutions. Note that Fischer could not prepare (benzene)(phenyl)methoxymethylene)dicarbonylchromium by substitution from (phenylmethoxymethylene)pentacarbonylchromium but only by nucleophilic addition followed by alkylation of (benzene)tricarboxylchromium.²¹ No products other than the arene complexes were isolated from the thermolysis reactions. In particular, no fluorene-type products derived from an alternative reaction pathway involving direct cyclization of the tetracarbonyl intermediate were observed, although indene-type products have been obtained in related systems.^{37,38}

(34) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979.

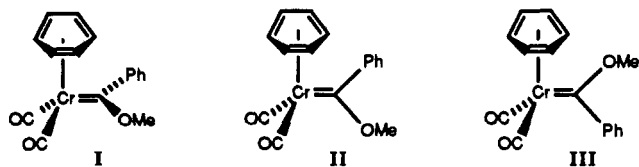
(35) See ref 2e, pp 247-264, and references therein.

(36) See, for example: (a) Fischer, E. O.; Fischer, H. *Chem. Ber.* 1974, 107, 657. (b) Fischer, E. O.; Fischer, H.; Werner, H. *Angew. Chem., Int. Ed. Engl.* 1972, 11, 644. (c) Dötz, K. H.; Sturm, W.; Popall, M.; Riede, J. *J. Organomet. Chem.* 1984, 277, 267. (d) Toledano, C. A.; Rudler, H.; Daran, J.-C.; Jeannin, Y. *J. Chem. Soc., Chem. Commun.* 1984, 574. (e) Casey, C. P.; Shusterman, A. J. *Organometallics* 1985, 4, 736.

(32) Foley, H. C.; Strubinger, L. M.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* 1983, 105, 3064.

(33) (a) Hegedus, L. S.; deWeck, G.; D'Andrea, S. *J. Am. Chem. Soc.* 1988, 110, 2122. (b) Hegedus, L. S.; Schwindt, M. A.; De Lombaert, S.; Imwinkelried, R. *J. Am. Chem. Soc.* 1990, 112, 2264. (c) Söderberg, B. C.; Hegedus, L. S.; Sierra, M. A. *J. Am. Chem. Soc.* 1990, 112, 4364. (d) Hegedus, L. S.; Imwinkelried, R.; Alarid-Sargent, M.; Dvorak, D.; Satoh, Y. *J. Am. Chem. Soc.* 1990, 112, 1109.

Another interesting aspect of complexes **3** and **5** arises from calculations performed by Kostic and Fenske on the conformational preferences of arene carbene complexes.³⁹ They compared the energies of arene complexes with horizontally (I) and vertically (II and III) oriented carbene



ligands and found that the horizontal conformer I was more stable by 8 kcal/mol. Their calculations were in contrast with those of Schilling, Hoffmann, and Lichtenberger⁴⁰ but were in agreement with the observed structure of (PhH)Cr(CO)₂C(OMe)Ph determined by Schubert.²² Kostic and Fenske applied the criterion of minimum orbital energy, rather than maximum orbital overlap, to predict the correct structure. Complexes **3** and **5** are thus locked in the high-energy vertical conformation by the linkage of the aryl rings. A consequence of this geometry is that there is better π back-bonding from the metal to the carbene carbon from interaction of the a'' , rather than the $2a'$, orbital on the metal fragment with the carbene p orbital.³⁹ Additionally, second-order orbital interactions between the filled metal $2a'$ orbital and the carbene carbon to oxygen σ^* orbital in complex **3** may also serve to enhance back-bonding to the carbene carbon.⁴¹ This analysis ignores effects due to the enforced syn eclipsed conformation between the CO ligands and the complexed arene ring, but these are expected to have only a minor contribution to the overall energy.⁴²

Supporting evidence for these orbital interactions comes from the observed bond lengths. The metal to carbene carbon bond lengths of 1.953 Å for **3** and 2.047 Å for **5** are short compared to those in typical alkoxy (2.0–2.1 Å) and amino (2.1–2.2 Å) carbene complexes.³¹ In contrast, the metal to carbonyl carbon bonds (1.84 Å for **3** and 1.83 Å for **5**) are long in comparison to the usual lengths of 1.80 Å, indicative of reduced π back-bonding. The observed carbene carbon to oxygen bond length of 1.354 Å in **3** can also be compared with bond lengths of 1.32–1.33 Å for typical chromium carbene complexes and bond lengths of 1.35–1.37 Å for complexes with diminished interactions between the oxygen and carbene carbon atoms.³¹

These orbital interactions are also evidenced by unusual ¹³C NMR resonances observed for these complexes. The ¹³C NMR signals for the carbene (321.2 ppm) and carbonyl carbons (247.2 ppm) in complex **3** are high-field-shifted and low-field-shifted, respectively, by about 25 ppm compared to those for known Fischer pentacarbonyl carbene⁴³ and arene dicarbonyl carbene complexes.²¹ These shifts

arise from enhanced back-bonding to the carbene ligand, which would increase electron density at the carbene carbon, shifting the ¹³C resonance upfield, and reduce back-bonding to the carbonyl groups, shifting their ¹³C resonances downfield. The ¹³C NMR signal for the carbonyl carbons (245.7 ppm) in complex **5** is also low-field-shifted by about 25 ppm compared to [(dimethylamino)phenylmethylene]pentacarbonylchromium.⁴³ However, the carbene carbon signal at 290.9 ppm is fairly typical for aminocarbene complexes.⁴³ Presumably, enhanced back-bonding from the metal only offsets the diminished interaction between the carbene carbon and the dimethylamino moiety, which are twisted away from optimal alignment.

The lack of reactivity of the complexes was surprising. Calculations found the LUMO's of arene carbene complexes to be the metal–carbene π -antibonding orbitals, as expected.^{39,40} Thus, it was predicted that the complexes would be subject to frontier-controlled nucleophilic additions to the carbene carbons. Nonetheless, this was not observed. Presumably, the geometry-enforced electronic perturbation of the complex, characterized by a more favorable orbital overlap between the metal fragment and the carbene ligand, renders the carbene carbon less electrophilic. Steric factors may also contribute to decreased reactivity at the carbene carbon, whereby the hydrogen atoms at the 2- and 6-positions on the complexed arene ring shield the carbene carbon. Electronic factors must also dictate the reactivity of the chromium-complexed arene ring. Compared to typical (arene)chromium tricarbonyl complexes, the conversion of a CO ligand to the poorer π -accepting carbene moiety in **3** and **5** must be sufficient to render the complexes inert to both deprotonation and nucleophilic attack. A similar effect is seen in the reactivity of phosphine-substituted (arene)chromium dicarbonyl complexes.⁴⁴

Conclusions

We have demonstrated that thermolysis of methoxy and dimethylamino biphenyl chromium carbene complexes generates cyclic arene carbene complexes. These novel structures contain the carbene moiety in a high-energy vertical conformation, which serves to enhance π back-bonding from the metal fragment to the carbene carbon. This is supported by spectroscopic and X-ray crystal structure data. The complexes are resistant to nucleophilic attack and deprotonation by lithium reagents. We are now exploring the contrasts between photochemical and thermal reaction behavior in other Fischer carbene complexes.

Experimental Section

All reactions were carried out under nitrogen by standard Schlenk-tube techniques, unless noted otherwise. Diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane and hexane were distilled from calcium hydride. All other reagents were used as received. Flash chromatography was performed on Merck silica gel 60 (230–400 mesh). Infrared spectra were recorded on a Perkin-Elmer 1600 FT-infrared spectrometer. ¹H and ¹³C NMR spectra were recorded on Bruker AF 200, AM 360, and AM 500 spectrometers. Chemical shifts are reported in ppm with Me₄Si or CDCl₃ as internal standards. Mass spectra were recorded at 70 eV on an AEI MS902 instrument. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

[(1,1'-Biphenyl-2-yl)methoxymethylene]pentacarbonylchromium (**1**). A 1.7 M pentane solution of *tert*-butyllithium (27 mL, 46.2 mmol) was added to a solution of 2-iodobiphenyl (6.18 g, 22 mmol) in ether (70 mL), and the milky solution was

(37) (a) Dötz, K. H.; Neugebauer, P. *Angew. Chem., Int. Ed. Engl.* 1978, 17, 851. (b) Dötz, K. H.; Pruski, I. *Chem. Ber.* 1978, 111, 2059. (c) Aumann, R.; Heinen, H.; Hinterding, P.; Sträter, N.; Krebs, B. *Chem. Ber.* 1991, 124, 1229.

(38) Preliminary results from our laboratories indicate that five-membered-ring products can be selectively obtained from thermolysis of certain dienyl carbene complexes.

(39) Kostic, N. M.; Fenske, R. F. *J. Am. Chem. Soc.* 1982, 104, 3879.

(40) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* 1979, 101, 585.

(41) For an example of this effect, see: Fischer, E. O.; Kleine, W.; Schambeck, W.; Schubert, U. *Z. Naturforsch., B* 1982, 36, 1575.

(42) (a) Jackson, W. R.; Jennings, W. B.; Rennison, S. C.; Spratt, R. *J. Chem. Soc. B* 1969, 1214. (b) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* 1977, 99, 7546.

(43) Hafner, A.; Hegedus, L. S.; deWeck, G.; Hawkins, B.; Dötz, K. H. *J. Am. Chem. Soc.* 1988, 110, 8413.

(44) Iwata, R.; Ogata, I. *Nippon Kagaku Zasshi* 1969, 90, 1156.

stirred for 1.5 h at $-78\text{ }^\circ\text{C}$ and 0.5 h at $0\text{ }^\circ\text{C}$. The resulting yellow solution was slowly transferred via cannula into a suspension of chromium hexacarbonyl (4.62 g, 21 mmol) in ether (150 mL) at room temperature. The yellow-orange solution was stirred for 30 min after complete addition and cooled to $0\text{ }^\circ\text{C}$. A saturated aqueous sodium bicarbonate solution (2 mL) was added, followed by rapid addition of methyl triflate (3.0 mL, 26.4 mmol). After the mixture was stirred at room temperature for 30 min, the reaction was quenched with saturated aqueous sodium bicarbonate solution (20 mL) and saturated aqueous potassium carbonate solution (5 mL). The organic layer was separated and dried (MgSO_4), and the solvents were removed in vacuo. The resulting red oil was recrystallized from hexane at $-20\text{ }^\circ\text{C}$ to provide 6.026 g of orange-red crystals. The mother liquor was purified via silica gel chromatography (95:5 hexane/ethyl acetate) to provide a further 1.780 g of the carbene product for a total combined yield of 96%. $^1\text{H NMR}$ (CDCl_3 , 360 MHz, at $50\text{ }^\circ\text{C}$): δ 4.46 (3 H, s), 7.00 (1 H, d, $J = 7.1$ Hz), 7.21–7.25 (2 H, m), 7.29–7.42 (6 H, m). $^{13}\text{C NMR}$ (CDCl_3 , 50 MHz): δ 66.8, 120.7 (br), 127.0, 127.8, 128.5 (2 C), 129.2, 130.8, 133.8, 139.9, 152.9 (br), 215.5, 224.2, 356.7. IR (CDCl_3): 3064, 3019, 2954, 2840, 2064 (sh, CO), 1982 (w, CO), 1949 (vs, CO), 1470, 1448, 1435, 1268, 1240, 1212, 1180, 1140, 1107, 1075 cm^{-1} . Anal. Calcd for $\text{C}_{19}\text{H}_{12}\text{CrO}_6$: C, 58.77; H, 3.11. Found: C, 58.78; H, 3.32. MS (70 eV): m/e 388 (6, M^+), 360 (1, $\text{M}^+ - \text{CO}$), 304 (47, $\text{M}^+ - 3\text{CO}$), 276 (6, $\text{M}^+ - 4\text{CO}$), 248 (100, $\text{M}^+ - 5\text{CO}$), 218 (7), 206 (48), 205 (59). MS (16 eV): m/e 388 (5, M^+), 304 (92, $\text{M}^+ - 3\text{CO}$), 248 (100, $\text{M}^+ - 5\text{CO}$).

9-Hydroxy-10-methoxyphenanthrene (2). A solution of carbene complex 1 (0.388 g, 1 mmol) in dry THF (250 mL) was photolyzed for 2 h with a 450-W medium-pressure mercury lamp with a Pyrex filter while slowly sparging with CO. The yellow solution was let stand overnight under 1 atm of CO to effect decomplexation of the product from its tricarbonylchromium complex. The resulting colorless solution was concentrated in vacuo, and the residue was purified by flash chromatography on silica gel. Elution with hexane provided 0.137 g (62%) of hexacarbonylchromium as a white powder. Further elution with hexane and ethyl acetate (90:10) yielded 0.202 g (90%) of product 2 as a white solid. $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 3.97 (3 H, s), 6.26 (1 H, s), 7.52 (1 H, td, $J = 7.6, 0.9$ Hz), 7.60–7.65 (3 H, m), 8.01 (1 H, d, $J = 8.0$ Hz), 8.30–8.32 (1 H, m), 8.60–8.62 (2 H, m). $^{13}\text{C NMR}$ (CDCl_3 , 90 MHz): δ 61.3, 120.8, 122.4, 122.5, 123.0, 124.3, 125.5, 126.3, 126.6, 126.9, 127.0, 127.5, 128.6, 136.0, 140.9. IR (CDCl_3): 3534 (OH), 3080, 2941, 2838, 1634, 1607, 1502, 1453, 1413, 1354, 1289, 1266, 1220, 1164, 1055, 1032 cm^{-1} . HRMS: calcd for $\text{C}_{15}\text{H}_{12}\text{O}_2$ 224.0837, found 224.0830. MS: m/e 224 (100, M^+), 209 (92), 188 (56), 181 (43), 173 (50), 165 (9), 163 (9), 152 (44), 126 (5), 104 (6), 76 (9), 32 (14). Anal. Calcd for $\text{C}_{15}\text{H}_{12}\text{O}_2$: C, 80.34; H, 5.39. Found: C, 80.15; H, 5.52.

[(1',2',3',4',5',6'- η)-1,1'-Biphenyl-2-yl]methoxymethylene]dicarbonylchromium (3). A solution of complex 1 (0.388 g, 1.0 mmol) in THF (50 mL) was refluxed for 36 h. The resulting dark solution was concentrated and the residue purified via silica gel chromatography (90:10 hexane/ethyl acetate) to provide 0.273 g (90%) of the arene carbene complex as a black microcrystalline solid. X-ray-quality crystals could be obtained by recrystallization from hexane and dichloromethane. $^1\text{H NMR}$ (CDCl_3 , 360 MHz): δ 4.47 (3 H, s), 5.40 (2 H, dd, $J = 6.5, 1.0$ Hz), 5.46 (1 H, td, $J = 6.3, 1.0$ Hz), 5.66 (2 H, t, $J = 6.4$ Hz), 7.26–7.33 (3 H, m), 7.39–7.42 (1 H, m). $^{13}\text{C NMR}$ (CD_3COCD_3 , 50 MHz): δ 63.3, 94.6, 102.4, 109.7, 114.5, 124.4, 127.2, 128.8, 129.1, 144.2, 160.1, 247.2, 321.2. IR (hexane; CO only): 1926, 1870 cm^{-1} . Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{CrO}_3$: C, 63.16; H, 3.98. Found: C, 63.40; H, 4.19.

[(1,1'-Biphenyl-2-yl)(dimethylamino)methylene]pentacarbonylchromium (4). A solution of 1 (1.50 g, 3.86 mmol), in THF (10 mL) was cooled to $-78\text{ }^\circ\text{C}$ in a dry ice/acetone bath. Dimethylamine (0.73 mL, 11.0 mmol) was added via a precooled syringe. Sodium methoxide (0.27 g, 5.0 mmol) was added to the above mixture all at once. After 20 min, the reaction was quenched with a saturated solution of NaHCO_3 (20 mL). The mixture was warmed to room temperature and extracted twice with Et_2O (50 mL + 20 mL). The organic layers were combined, dried (MgSO_4), and filtered through a plug of silica gel. The solvents were removed in vacuo. The resulting yellow oil was crystallized from Et_2O at $-20\text{ }^\circ\text{C}$ to provide 1.22 g of yellow crystals. The mother liquor was purified via silica gel chromatography (85:15 hex-

Table V. Crystal and Refinement Data for Complexes 3 and 5

	3	5
formula	$\text{C}_{16}\text{H}_{12}\text{CrO}_3$	$\text{C}_{17}\text{H}_{15}\text{CrNO}_2$
fw	304.26	317.31
cryst syst	monoclinic	monoclinic
space group	$C2/c$	$P2_1/n$
cryst dimens, mm	0.40×0.25 $\times 0.20$	0.35×0.20 $\times 0.20$
cryst color	black	black
cryst habit	rectangular	rectangular
a, Å	16.154 (2)	11.47 (1)
b, Å	12.256 (2)	7.082 (7)
c, Å	15.575 (2)	20.87 (2)
β , deg	122.92 (1)	108.13 (2)
Z	8	4
V , Å ³	2588.36	1610.50
ρ (calcd), g cm^{-3}	1.56	1.18
radiation (λ , Å)	Mo $K\alpha$ (0.7107)	Mo $K\alpha$ (0.7107)
$F(000)$, e	1248	592
temp, K	133	125
diffractometer	Picker (Crystal Logic)	Picker (Crystal Logic)
scan mode; speed, deg/min	$\theta-2\theta$; 3.0	$\theta-2\theta$; 3.0
2θ range, deg	1–50	1–45
total no. of data colld, no. of unique data used	4705, 2074 ($I >$ $3\sigma(I)$)	2494, 1580 ($I >$ $3\sigma(I)$)
no. of params refined	181	190
final shift/error, max and av	0.020, 0.003	0.009, 0.001
$R = \sum F_o - F_c / \sum F_o $	0.028	0.066
$R_w = (\sum w(F_o - F_c)^2 / \sum w(F_o)^2)^{1/2}$	0.050	0.101
$\text{GOF} = (\sum w(F_o - F_c)^2 / (N_o - N_v))^{1/2}$	2.069	3.113

ane/ethyl acetate) to provide a further 0.262 g of the aminocarbene product for a total combined yield of 96%. $^1\text{H NMR}$ (CDCl_3 , 200 MHz): δ 3.13 (3 H, s), 3.85 (3 H, s), 6.85 (1 H, d, $J = 7.3$ Hz), 7.23–7.42 (8 H, m). $^{13}\text{C NMR}$ (CDCl_3 , 50 MHz): δ 46.7, 51.2, 120.5, 126.8, 127.4, 127.6, 128.3, 128.8, 131.0, 131.6, 140.1, 150.9, 216.8, 223.6, 277.1. IR (CDCl_3 ; CO only): 2054 (sh, m), 1974 (w), 1926 (vs) cm^{-1} . HRMS: calcd for $\text{C}_{20}\text{H}_{15}\text{CrNO}_5$ 401.0355, found 401.0358. MS: m/e 401 (10, M^+), 373 (9, $\text{M}^+ - \text{CO}$), 345 (22, $\text{M}^+ - 2\text{CO}$), 317 (58, $\text{M}^+ - 3\text{CO}$), 289 (54, $\text{M}^+ - 4\text{CO}$), 261 (100, $\text{M}^+ - 5\text{CO}$), 233 (30), 231 (48), 225 (16), 218 (53), 208 (45), 205 (59).

[(1',2',3',4',5',6'- η)-1,1'-Biphenyl-2-yl](dimethylamino)methylene]dicarbonylchromium (5). A solution of complex 4 (0.50 g, 1.25 mmol) in 1,4-dioxane (150 mL) was gently refluxed at $105\text{ }^\circ\text{C}$ for 52 h with slow sparging of N_2 via a dispersion tube. The reaction was monitored by IR spectroscopy of the crude reaction mixture for the disappearance of starting complex 4. The resulting dark solution was concentrated and the residue purified via silica gel chromatography at $-40\text{ }^\circ\text{C}$ (85:15 hexane/ethyl acetate) to provide 0.116 g (29%) of the arene carbene complex as a purple waxy solid. X-ray-quality crystals were obtained by recrystallization from hexane and ethyl acetate. $^1\text{H NMR}$ (CDCl_3 , 360 MHz): δ 3.49 (3 H, br s), 3.64 (3 H, br s), 4.59 (1 H, t, $J = 6.1$ Hz), 5.15 (2 H, d, $J = 5.8$ Hz), 5.27 (2 H, t, $J = 6.1$ Hz), 6.80–6.90 (1 H, m), 7.13–7.19 (2 H, m), 7.28–7.32 (1 H, m). $^{13}\text{C NMR}$ (CD_3COCD_3 , 50 MHz): δ 47.9 (br), 52.2 (br), 86.1, 94.1, 99.4, 118.6, 119.7, 124.5, 126.2, 127.7, 145.8, 156.5, 245.7, 290.9. IR (hexane; CO only): 1885, 1820 cm^{-1} . HRMS: calcd for $\text{C}_{17}\text{H}_{15}\text{CrNO}_2$ 317.0508, found 317.0535. MS: m/e 317 (69, M^+), 289 (13, $\text{M}^+ - \text{CO}$), 261 (100, $\text{M}^+ - 2\text{CO}$), 232 (18), 218 (15), 205 (33), 165 (10), 152 (9).

General Methods of Crystallographic Analyses. All data were collected on a modified Picker FACS-1 diffractometer.⁴⁵ All calculations were performed on the UCLA departmental VAX 3100 cluster using the UCLA Crystallographic Package (locally edited versions of REDUCE, SHELXS-86, ORFLS, ORFFE, HYDROGEN, ORTEP, and PUBLIST). Scattering factors and corrections for anomalous dispersion components were obtained from ref 46.

(45) Strouse, C. E. *Rev. Sci. Instrum.* 1976, 47, 871.

Details of the individual data collections are given in Table V. Selected results are presented in Tables I-IV, while full crystallographic data appear in Tables S1-S10 in the supplementary material.

X-ray Structure Determination of Compounds 3 and 5. Suitable crystals for X-ray structural analysis of compound 3 (black, rectangular, $0.40 \times 0.25 \times 0.20$ mm) and 5 (black, rectangular, $0.35 \times 0.20 \times 0.20$ mm) were glued to the tips of glass fibers. The crystals were mounted and optically centered on a modified Picker four-circle diffractometer equipped with a gas-stream low-temperature device and graphite-monochromatized Mo source.⁴⁵ Accurate unit cell parameters and orientation matrices were obtained by a least-squares fit to the automatically centered settings of 38 reflections for 3 and 28 reflections for 5, respectively, and are listed in Table V together with other experimental details. A $\theta/2\theta$ scan mode was employed to collect one hemisphere ($h, \pm k, \pm l$) of data with the maximum 2θ of 50° for 3 and one quadrant ($h, k, \pm l$) of data with the maximum 2θ of 45° for 5, at low temperature (128 K). Three standard reflections were monitored for every 97 reflections collected and showed no significant variations throughout the data collection. Intensities were derived from an analysis of scan profiles. The data were corrected for Lorentz and polarization effects. A ψ -scan procedure was used for an empirical absorption correction.

The structures were solved in the monoclinic space groups $C2/c$ for 3 and $P2_1/n$ (No. 14) for 5 by heavy-atom methods of SHELX86,

(46) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

which revealed the positions of chromium and most of the carbon atoms. The remaining non-hydrogen atoms were located from subsequent difference electron density maps. This was followed by several cycles of full-matrix least-squares refinement. Hydrogen atoms were included as fixed contributors to the final refinement cycles. The positions of hydrogen atoms were calculated on the basis of idealized geometry and bond length (C-H = 1.00 Å). For methyl groups, at least one of the hydrogen atom positions was located from the difference-Fourier map.

For compound 3, in the final cycles of least-squares refinement, all non-hydrogen atoms were refined with anisotropic thermal coefficients. The refinement converged at $R = 0.031$ and $R_w = 0.053$. For compound 5, an unidentified disordered solvent molecule was located at the inversion center. Attempts to model the solvent molecule were not successful. Crystal-packing diagrams show the solvent molecules occupying channels down the inversion center. Three strong peaks with reasonable C-C distances were arbitrarily assigned as carbon atoms with half-occupancies and were included as fixed contributors in the final cycles of refinement. The final R factors are 0.066 and 0.101.

Acknowledgment. We thank the UCLA Academic Senate, Committee on Research, for support of this research.

Supplementary Material Available: Tables of positional parameters, bond distances, bond angles, and thermal parameters for compounds 3 and 5 (10 pages); listings of observed and calculated structure factors for compounds 3 and 5 (17 pages). Ordering information is given on any current masthead page.

Preparation of Symmetrical Di-1-alkynyl Tellurides and Diynes by Reduction of TeCl_4 with 1-Alkynyllithium Reagents

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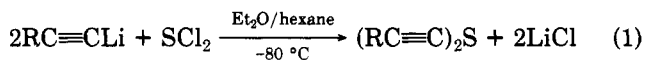
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Di-1-alkynyl tellurides ($(\text{RC}\equiv\text{C})_2\text{Te}$, where R = Me, Et, *n*-Pr, *t*-Bu, Me_3Si , Ph) have been prepared in 42-69% yields by the reaction of TeCl_4 with 4 equiv of the corresponding 1-alkynyllithium reagents ($\text{RC}\equiv\text{CLi}$). Diynes ($\text{RC}\equiv\text{CC}\equiv\text{CR}$, where R = *t*-Bu, Me_3Si , Ph) were isolated as major byproducts from these reactions. While tetra-1-alkynyltellurium(IV) or other possible organotellurium(IV) intermediates were not isolated, it is proposed that these intermediates decompose by a reductive-elimination pathway to afford $(\text{RC}\equiv\text{C})_2\text{Te}$ and $\text{RC}\equiv\text{CC}\equiv\text{CR}$. These organotellurium compounds have been characterized by IR and ^1H , ^{13}C , and ^{125}Te NMR spectroscopies.

Introduction

Organotellurium compounds have attracted a great deal of interest as useful reagents in organic chemistry.¹ Even though many diorganyl tellurides (R_2Te) have been extensively studied, little attention has been given to alkynyl tellurides until recently.² Di-1-alkynyl sulfides are readily obtainable from ether suspensions or solutions of 1-alkynyllithium reagents and sulfur dichloride (eq 1).³ Di-1-

propynyl selenide, $(\text{MeC}\equiv\text{C})_2\text{Se}$, was obtained in a good yield by reacting 1-propynyllithium with a cold solution



(1) (a) Irgolic, K. J. *The Organic Chemistry of Tellurium*; Gordon and Breach Science: New York, 1974. (b) Engman, L. *Acc. Chem. Res.* 1985, 18, 274. (c) Petragnani, N.; Comasseto, J. V. *Synthesis* 1986, 1. (d) Suzuki, H.; Hanazaki, Y. *Chem. Lett.* 1986, 549. (e) Suzuki, H.; Manabe, H.; Enokiya, R.; Hanazaki, Y. *Chem. Lett.* 1986, 1339. (f) Ohe, K.; Takahashi, H.; Uemura, S.; Sugita, N. *J. Org. Chem.* 1987, 52, 4859. (g) Sadekov, I. D.; Rivkin, B. B.; Minkin, V. I. *Russ. Chem. Rev. (Engl. Transl.)* 1987, 56, 342. (h) Huang, Y.-Z.; Shi, L.-L.; Li, S.-W.; Wen, X.-Q. *J. Chem. Soc., Perkin Trans. 1* 1989, 2397.

(2) (a) Dabdoub, M. J.; Comasseto, J. V. *Organometallics* 1988, 7, 84. (b) Dabdoub, M. J.; Comasseto, J. V.; Braga, A. L. *Synth. Commun.* 1988, 18, 1979. (c) Gedridge, R. W., Jr.; Higa, K. T.; Harris, D. C.; Nissan, R. A.; Nadler, M. P. *Organometallics* 1989, 8, 2812. (d) Dabdoub, M. J.; Comasseto, J. V.; Barros, S. M.; Moussa, F. *Synth. Commun.* 1990, 20, 2181. (e) Murai, T.; Imaeda, K.; Kajita, S.; Ishihara, H.; Kato, S. *J. Chem. Soc., Chem. Commun.* 1991, 832.

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