away from the open face, rather than in the endo-position from which a carbon insertion might be more easily obtained.

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Supplementary Material Available: Tables of positional parameters, anisotropic temperature factors, bond distances, and bond angles (8 pages). Ordering information is given on any current masthead page.

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Regioselective Synthesis of 2-Pyrones Mediated by Organometallic Dinitrosyl Cations of the Group 6 Metals[1]

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Summary: **The formally 16-electron cations $[Cp^*M(NO)_2]^+$ ($Cp^* = \eta^5\text{-}C_5Me_5$, M = Cr, Mo, W) mediate the regioselective and stoichiometric assembly of iodopyrones, $I\overline{C{=}C(H)C(R){=}C(Ph)OC}{=}O$ (R = Et, Me), from methyl propiolate, $HC{\equiv}C{-}CO_2Me$, phenylacetylenes, $RC{\equiv}CPh$, and I_2. Intermediate organometallic complexes formed during these processes have been isolated and fully characterized.**

The 2-pyrone group occurs in a variety of naturally occurring compounds, many of which exhibit important biological activity. For instance, Kava resin contains a large number of substituted 2-pyrones which display a wide range of pharmacological properties.[2] Furthermore, derivatives of 2-pyrones are known to act as human elastase inhibitors.[3,4] Some 2-pyrone species also exhibit antihistamine, antibiotic, and antiulcer activity, and 2-pyrones have been cited as potential agents for treatment of psoriasis.[5] In addition, 2-pyrones are valuable intermediates in their own right for various organic conversions. The versatile reactivity of 2-pyrones in Diels–Alder reactions is well documented.[6] During these latter conversions they can act as either dienes or dienophiles, and initially formed products may undergo subsequent thermal conversions, thereby affording species such as substituted benzenes and polycyclic compounds.

Although many syntheses of 2-pyrones are known,[6] relatively few employ transition-metal compounds as catalysts or mediators.[7-10] We now wish to report that the formally 16-electron cations, $[Cp^*M(NO)_2]^+$ ($Cp^* = \eta^5\text{-}C_5Me_5$, M = Cr, Mo, W), mediate the regioselective and stoichiometric assembly of iodopyrones, $I\overline{C{=}C(H)C(R){=}C(Ph)OC}{=}O$ (R = Et, Me), from methyl propiolate, $HC{\equiv}C{-}CO_2Me$, phenylacetylenes, $RC{\equiv}CPh$, and I_2 in the metals coordination spheres. Furthermore, we have been able to effect these conversions in a stepwise fashion and have succeeded in isolating and fully characterizing the intermediate organometallic complexes.

Experimental Section

All reactions and subsequent manipulations involving organometallic reagents were performed under anhydrous and anaerobic conditions using conventional drybox and vacuum-line Schlenk techniques under an atmosphere of dinitrogen unless specified otherwise.[11,12] Solvents were dried, distilled, and deaerated with N_2 prior to use. All reagents were purchased from commerical suppliers or were prepared according to published procedures. General procedures routinely employed in these laboratories have been described in detail elsewhere.[13]

IR spectra were recorded on a Nicolet Model 5DX FT-IR spectrometer, internally calibrated by a He/Ne laser. ^1H NMR spectra were recorded on a Bruker AM-200E spectrometer; chemical shifts are reported in parts per million downfield from tetramethylsilane, referenced to the residual proton signal of the solvent employed. Low-resolution mass spectra (EI, 70 eV) were obtained on a Kratos MS50 spectrometer using the direct insertion method by Dr. G. K. Eigendorf and the staff of the UBC Mass Spectrometry Laboratory. Elemental analyses were performed by Mr. P. Borda at the University of British Columbia.

The preparations of the $[Cp^*M(NO)_2]BF_4$ complexes, complex salts **1a–c**, and compounds **2a–c** were effected in a similar manner. The procedures for the complete series of transformations involving the chromium complexes are outlined below as representative examples.

Generation of a Dichloromethane Solution of $[Cp^*Cr(NO)_2]BF_4$. $AgBF_4$ (0.38 g, 2.0 mmol) was added to a stirred, brown solution of $Cp^*Cr(NO)_2Cl$[14] (0.55 g, 1.9 mmol) in CH_2Cl_2

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Table I. Mass Spectral and Elemental Analysis Data for Complexes 1–3

complex	MS m/z	anal. found (calcd) C	H	N
1a		52.41 (52.57)	5.30 (5.33)	4.99 (5.11)
1b		47.49 (47.77)	4.66 (4.72)	4.72 (4.85)
1c		41.07 (41.47)	4.07 (4.09)	4.11 (4.21)
2a	446 [P^+] 416 [$P^+ - NO$] 386 [$P^+ - 2NO$]	61.71 (61.88)	6.00 (5.87)	6.14 (6.27)
2b	448 [$P^+ - NO$]	55.20 (55.46)	5.10 (5.09)	6.00 (5.88)
2c	464 [P^+]	46.56 (46.83)	4.26 (4.29)	4.89 (4.96)
3a	326 [P^+]	47.80 (47.88)	3.37 (3.40)	0.00 (0.00)

(35 mL). Monitoring of the progess of the reaction by IR spectroscopy showed it to be complete after 15 min, as the nitrosyl bands of the reactant at 1782 and 1684 cm^{-1} were replaced by absorptions at 1809 and 1709 cm^{-1}, characteristic of $[Cp^*Cr(NO)_2]^+$.[15] The reaction mixture deposited a white precipitate which was removed by filtration of the mixture through Celite (2 × 4 cm) supported on a medium-porosity frit. Subsequent reaction of $[Cp^*Cr(NO)_2]BF_4$ was effected immediately without isolation of this species.

Reaction of $[Cp^*Cr(NO)_2]BF_4$ with Methyl Propiolate and 1-Phenyl-1-butyne. Methyl propiolate (1.0 mL, 11.2 mmol) and 1-phenyl-1-butyne (1.5 mL, 10.6 mmol) were added to a brown CH_2Cl_2 (50 mL) solution of $[Cp^*Cr(NO)_2]BF_4$ (1.9 mmol). After 15 h, the brown reaction mixture was concentrated in vacuo to about 5 mL, and Et_2O (50 mL) was added rapidly by syringe, operations which resulted in the precipitation of a green, microcrystalline solid. The supernatant solution was removed by filter cannulation, and the solid was washed with additional Et_2O (50 mL) and recrystallized from CH_2Cl_2/Et_2O to obtain 0.82 g (1.5 mmol, 77% yield) of $[Cp^*Cr(NO)_2\overline{C{=}C(H)C(Et){=}C(Ph)OC}{=}OMe]BF_4$ (**1a**). A crystal suitable for a single-crystal X-ray diffraction analysis was grown from an acetone solution of the salt into which pentane was allowed to diffuse at 7 °C over a period of 1 week. The analytical and spectroscopic data for all isolated pyrone complexes are collected in Tables I and II.

The reactions of $[Cp^*Mo(NO)_2]BF_4$ or $[Cp^*W(NO)_2]BF_4$ generated in situ with methyl propiolate and 1-phenyl-1-propyne occurred in a manner identical to that outlined above to afford $[Cp^*Mo(NO)_2\overline{C{=}C(H)C(Me){=}C(Ph)OC}{=}OMe]BF_4$ (**1b**) or $[Cp^*W(NO)_2\overline{C{=}C(H)C(Me){=}C(Ph)OC}{=}OMe]BF_4$ (**1c**) as light brown and green solids, respectively, in comparable yields.

Reaction of $[Cp^*Cr(NO)_2\overline{C{=}C(H)C(Et){=}C(Ph)OC}{=}OMe]BF_4$ with NaI. The pyrone salt **1a** (0.25 g, 0.46 mmol) was dissolved in acetone (15 mL), and excess sodium iodide (0.35 g, 2.3 mmol) was added to the resulting brown solution. The reaction mixture was stirred for 15 min at ambient temperature. The solvent was then removed under reduced pressure, leaving a brown solid which was redissolved in Et_2O (30 mL). The Et_2O solution was filtered through alumina (1 × 4 cm, Woelm neutral, activity 1) supported on a medium-porosity frit. The column was washed with additional Et_2O (20 mL). Hexanes (20 mL) were added to the combined brown filtrates, and the solution was concentrated under vacuum until crystallization had been induced. This mixture was then allowed to stand at −20 °C overnight to complete the crystallization process. The resulting brown crystals were collected by filtration, washed with hexanes (2 × 5 mL), and dried in vacuo to obtain 0.15 g (0.34 mmol, 75% yield) of $Cp^*Cr(NO)_2\overline{C{=}C(H)C(Et){=}C(Ph)OC}{=}O$ (**2a**).

The compounds $Cp^*Mo(NO)_2\overline{C{=}C(H)C(Me){=}C(Ph)OC}{=}O$ (**2b**) and $Cp^*W(NO)_2\overline{C{=}C(H)C(Me){=}C(Ph)OC}{=}O$ (**2c**) were prepared in similar yields from their complex salt precursors in a similar manner. Crystals of compound **2b** suitable for a single-crystal X-ray crystallographic analysis were obtained by slow evaporation of a saturated Et_2O solution of the species at room temperature for 2 h.

Table II. ^1H NMR and IR Data for Complexes 1–3

complex	^1H NMR (δ)[a]	IR (Nujol) ν_{NO}	$\nu_{C=O}$
1a	8.15 (s, 1 H, $=C(H)$)	1755	1713
	7.80–7.50 (m, 5 H, C_6H_5)	1678	
	4.43 (s, 3 H, $=OCH_3$)		
	2.75 (q, 2 H, CH_2CH_3)		
	1.82 (s, 15 H, $C_5(CH_3)_5$)		
	1.27 (t, 3 H, CH_2CH_3)		
1b	8.71 (s, 1 H, $=C(H)$)	1721	1640 (sh)
	8.07–7.61 (m, 5 H, C_6H_5)	1640	
	4.61 (s, 3 H, $=OCH_3$)		
	2.56 (s, 3 H, $=C(CH_3)$)		
	2.00 (s, 15 H, $C_5(CH_3)_5$)		
1c	8.22 (s, 1 H, $=C(H)$)	1701	1626 (sh)
	7.95–7.50 (m, 5 H, C_6H_5)	1626	
	4.45 (s, 3 H, $=OCH_3$)		
	2.46 (s, 3 H, $=C(CH_3)$)		
	2.09 (s, 15 H, $C_5(CH_3)_5$)		
2a	7.60–7.40 (m, 5 H, C_6H_5)	1755	1682
	7.24 (s, 1 H, $=C(H)$)	1651	
	2.51 (q, 2 H, CH_2CH_3)		
	1.78 (s, 15 H, $C_5(CH_3)_5$)		
	1.18 (t, 3 H, CH_2CH_3)		
2b	7.70–7.25 (m, 6 H, C_6H_5 and $=C(H)$)	1726	1713
	2.13 (s, 3 H, $=C(CH_3)$)	1674	
	1.93 (s, 15 H, $C_5(CH_3)_5$)		
2c	7.70–7.30 (m, 6 H, C_6H_5 and $=C(H)$)	1694	1678
	2.12 (s, 3 H, $=C(CH_3)$)	1607	
	1.99 (s, 15 H, $C_5(CH_3)_5$)		
3a	7.91 (s, 1 H, $=C(H)$)		1750
	7.50–7.30 (m, 5 H, C_6H_5)		
	2.42 (q, 2 H, CH_2CH_3)		
	1.13 (t, 3 H, CH_2CH_3)		

[a] All chemical shifts are reported as $CDCl_3$ solutions except for those of complex **1b**, which are given as an acetone-d_6 solution.

Synthesis of $I\overline{C{=}C(H)C(Et){=}C(Ph)OC}{=}O$ (3a). Elemental I_2 (0.34 g, 1.34 mmol) was added to a brown solution of neutral pyrone complex **2a** (0.60 g, 1.34 mmol) in Et_2O (50 mL). After being stirred at room temperature for 15 h, the reaction mixture was taken to dryness, and the resulting brown residue was extracted with pentane (50 mL). Cooling of this solution to −20 °C overnight afforded a mixture of brown and yellow crystals. The brown crystals were identified as $Cp^*Cr(NO)_2I$ by comparison of their spectroscopic properties with those exhibited by an authentic sample: IR (Nujol mull) ν_{NO} 1775 (s), 1682 (s) cm^{-1}; low-resolution mass spectrum (probe temperature 120 °C) m/z 374 [P^+], 344 [$P^+ - NO$], 314 [$P^+ - 2NO$]. The yellow crystals were recrystallized once from pentane and were identified as $I\overline{C{=}C(H)C(Et){=}C(Ph)OC}{=}O$. The isolated yield of this latter product was 0.32 g (0.98 mmol, 73%), and its analytical and spectroscopic data are also presented in Tables I and II.

Synthesis of $I\overline{C{=}C(H)C(Me){=}C(Ph)OC}{=}O$ (3b). An equimolar amount of elemental I_2 was reacted with the neutral pyrone complexes **2b** and **2c** in an NMR tube using $CDCl_3$ as the solvent. The ^1H NMR spectra of the resulting solutions each exhibited only the signals assignable either to the appropriate $Cp^*M(NO)_2I$ species or to the expected free iodopyrone. The pyrone formed and its resulting signals were identical in both experiments.

Reaction with **2b**: ^1H NMR ($CDCl_3$) δ 7.91 (s, 1 H, $=C(H)$), 7.65–7.35 (m, 5 H, C_6H_5), 2.14 (s, 3 H, CH_3), 1.99 (s, 15 H, $C_5(CH_3)_5$).

Reaction with **2c**: ^1H NMR ($CDCl_3$) δ 7.91 (s, 1 H, $=C(H)$), 7.65–7.35 (m, 5 H, C_6H_5), 2.14 (s, 3 H, CH_3), 2.08 (s, 15 H, $C_5(CH_3)_5$).

X-ray Crystallographic Analysis of $[Cp^*Cr(NO)_2\overline{C{=}C(H)C(Et){=}C(Ph)OC}{=}OMe]BF_4$ (1a). A green crystal of **1a** was mounted in a Lindemann capillary tube using vacuum grease as adhesive. Intensity data (Mo Kα/graphite monochromator) were collected at 195 K using an Enraf-Nonius CAD-4F dif-

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(14) The $Cp^*M(NO)_2Cl$ complexes for M = Cr, Mo were synthesized in a manner similar to that employed for the congeneric tungsten species.[15]

(15) Legzdins, P.; Martin, D. T. *Organometallics* **1983**, 2, 1785.

fractometer with an extensively in-house-modified low-temperature system. The unit cell was determined from 25 well-centered reflections (28° ≤ 2θ ≤ 42°). Two intensity standards, measured every 1 h of exposure time, showed no systematic variations. The data were corrected analytically for the effects of absorption,[16] and data reduction also included Lorentz and polarization corrections.

The position of the chromium atom was deduced from the Patterson map and the rest of the non-hydrogen atom positions were located in subsequent Fourier maps. After refinement of all non-hydrogen atoms with isotropic thermal parameters, an electron density difference map showed peaks consistent with anisotropic thermal motion for the atoms in both the Cp*Cr(NO)$_2$ fragment and the BF_4^- ion. Refined anisotropic thermal parameters for these atoms suggested unreasonably extreme anisotropic thermal motion or disorder corresponding to a pivotal displacement of the entire fragment about an axis parallel to the Cr–C(6) bond and passing close to C(3). Subsequently, the atoms of this unit were each modeled isotropically on two fractionally occupied sites with the aid of soft restraints to stabilize the least-squares refinement and maintain chemical reasonableness. The relative occupancy for the two components was refined such that the net occupancy was 1. A single isotropic thermal parameter was refined for each disordered pair of Cr, N, and O atoms and for each pair of the two types of carbon atoms in the Cp* group. All hydrogen atoms were placed in calculated positions (C–H 0.95 Å) and were assigned isotropic thermal parameters and site occupancies dependent on those for the corresponding carbon atoms. During refinement, the hydrogen atom coordinate shifts were linked with those of the carbon atoms to which they were bound. A single parameter was refined for the isotropic thermal motion of all hydrogen atoms. The atoms of the pyrone group were refined with individual isotropic thermal parameters. Finally, the disordered BF_4^- ion was most simply treated as three rigid groups of regular tetrahedral geometry having refined fractional occupancies restrained to total 1. A single thermal parameter was refined each for boron and for fluorine. Final full-matrix least-squares refinement included 185 parameters for 1691 data ($I_o \geq 2.5\sigma(I_o)$) and 101 restraints. Structures of either hand were refined to convergence, and the one with the lower residual is reported. With unit weights, $\langle w(|F_o| - |F_c|)^2\rangle$ was near constant as a function of both $|F_o|$ and $[(\sin\theta)/\lambda]^2$, and therefore no other weighting scheme was applied.

Complex scattering factors for neutral atoms[17] were used in the calculation of structural factors. The programs used for data reduction, structure solution, and initial refinement were from the NRCVAX Crystal Structure System.[18] The program suite CRYSTALS[19] was employed in the final refinement involving restraints. All computations were carried out on a MICROVAX-II computer.

X-ray Crystallographic Analysis of Cp*Mo(NO)$_2$C=C(H)C(Me)=C(Ph)OC=O (2b). A dark amber crystal was mounted on a Pyrex filament and thinly coated with epoxy resin. Intensity data were collected with an Enraf-Nonius CAD-4F diffractometer. The unit cell was determined from 25 well-centered reflections (36° ≤ 2θ ≤ 42°). Two intensity standards were measured every 1.3 h of acquisition time and showed no significant variations during the course of data acquisition. The data were corrected analytically for absorption.[16] Data reduction also included Lorentz and polarization corrections.

The structure was solved by standard Patterson/Fourier synthesis methods. Hydrogen atoms were placed in calculated positions and assigned isotropic thermal parameters initially 10% larger than those for the corresponding carbon atoms. The orientations of the methyl groups were initially assigned on the basis of reasonably placed peaks from an electron-density difference map. The CH_3 fragments of the Cp* ligand were refined as rigid groups, but the coordinates of the hydrogen atoms of the methyl group (C(19)) on the pyrone ring were independently refined. A total of 21 soft-distance restraints were applied which required the hydrogen atoms on each methyl group to be approximately symmetrically disposed about the C–CH_3 bond axis. The coordinates of the non-methyl hydrogen atoms were linked with those of their respective carbon atoms. A single least-squares parameter was refined for the isotropic thermal motion of the hydrogen atoms. The final full-matrix least-squares refinement of 293 parameters for 2990 data, $I_o \geq 2.5\sigma(I_o)$, included anisotropic thermal parameters for all non-hydrogen atoms. A weighting scheme based on counting statistics was applied such that $\langle w(|F_o| - |F_c|)^2\rangle$ was nearly constant as a function of both $|F_o|$ and $[(\sin\theta)/\lambda]^2$.

Table III. Crystallographic and Experimental Data for Complexes 1a and 2b

	1a	2b
color	green	amber
formula	$C_{24}H_{29}N_2BFO_4Cr$	$C_{22}H_{24}N_2O_4W$
fw	548.3	476.38
cryst syst	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1/c$
a (Å)	8.270 (2)	16.581 (2)
b (Å)	9.063 (1)	8.937 (1)
c (Å)	34.437 (4)	15.220 (2)
α (deg)	90	90
β (deg)	90	107.069 (9)
γ (deg)	90	90
V (Å^3)	2581.1	2156.0
Z	4	4
θ_c (g/cm^3)	1.411	1.468
$F(000)$	1135.8	975.70
μ(MoKα) (cm^{-1})	4.9	6.2
T (K)	195	293
cryst dimens (mm)	0.22 × 0.24 × 0.29	0.20 × 0.24 × 0.41
transm factors	0.89–0.92	0.862–0.898
scan type	ω	ω–2θ
scan range (deg)	0.8 + 0.35 tan θ	0.75 + 0.35 tan θ
scan speed (deg/min)	0.57–3.30	0.68–5.5
2θ limits (deg)	$4 \leq 2\theta \leq 50$	$4 \leq 2\theta \leq 50$
no. of unique reflns	2618	3754
no. of reflns with $I_o > 2.5\sigma(I_o)$	1691	2990
no. of variables	185	293
R_F[a]	0.054	0.021
R_{wF}[b]	0.056	0.029
max |shift/error|	0.07	0.08
residual density (e/Å^3)	0.36 (7)	0.23 (5)

[a] $R_F = \sum|(|F_o| - |F_c|)|/\sum|F_o|$. [b] $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

Rigid body analysis[20] of the anisotropic thermal parameters of the molecule yielded $R = 0.165$ for the agreement between observed and calculated U_{ij}. Internal motion was analyzed in terms of a segmented rigid body.[21] A model which included all the non-hydrogen atoms, except for the oxygen atoms of the nitrosyl groups, and in which the atoms of the Cp* and the pyrone groups were allowed internal libration about their bonding axes to Mo, gave $R = 0.079$ with an rms discrepancy of 0.003 Å^2. Comparison of the calculated and observed thermal parameters on an individual basis revealed significant excess motion (still unaccounted for) in the methyl carbon atoms of the Cp* group, the outer three carbon atoms of the phenyl group, N(2), and O(4). Corrections to the bond lengths based on this model, plus riding corrections for the Mo–N and N–O bond lengths, are included in Table VII. Various models involving further segmentation or different sets of atoms produced either no significant improvement over this model or were ill-conditioned. All further computations were carried out as per those of **1a** outlined above.

Pertinent crystallographic and experimental parameters for both **1a** and **2b** are summarized in Table III. The atomic coordinates and isotropic temperature factors for non-hydrogen atoms of complexes **1a** and **2b** are given in Tables IV and V, respectively.

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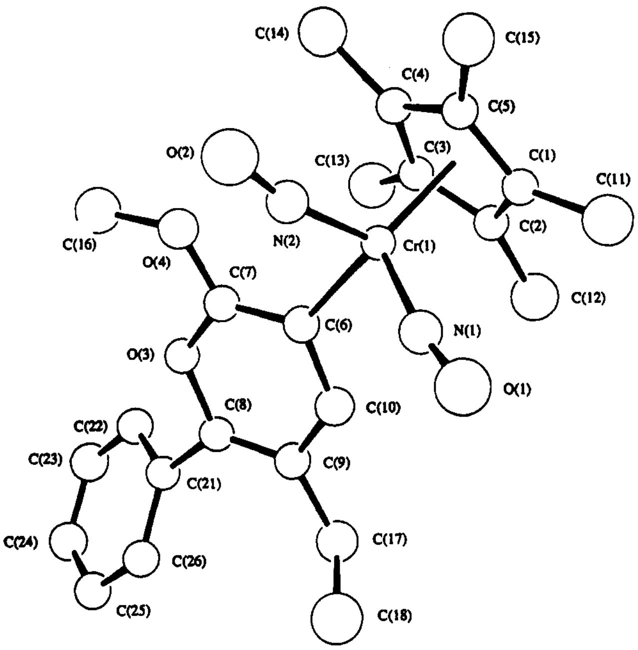
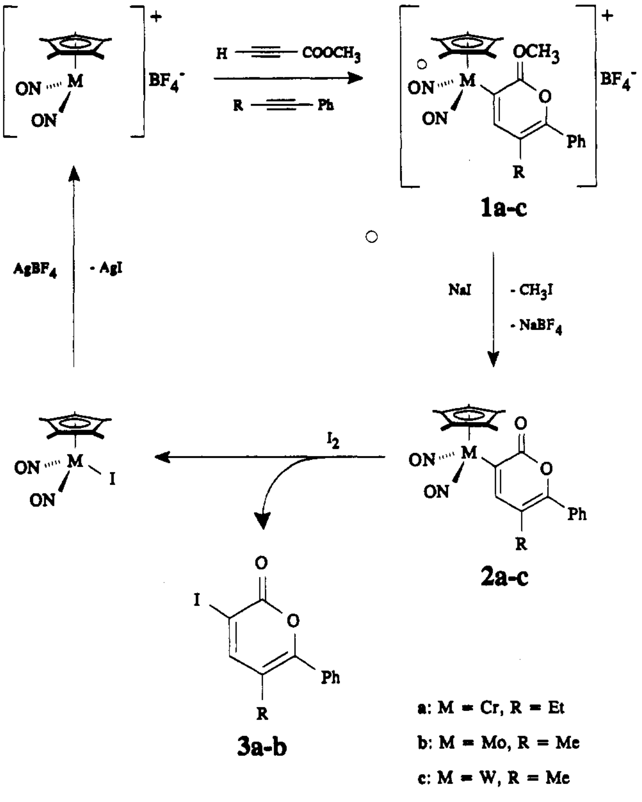


Figure 1. Solid-state molecular structure of the complex cation of **1a**, the hydrogen atoms having been omitted for clarity.

Scheme I



a: M = Cr, R = Et

b: M = Mo, R = Me

c: M = W, R = Me

Selected bond lengths (Å) and angles (deg) for the two complexes are presented in Tables VI and VII. The remaining molecular dimensions and thermal parameters (including non-hydrogen atom parameters) for both complexes are provided as supplementary material. Views of the solid-state molecular structures of complexes **1a** and **2b** are presented in Figures 1 and 2, respectively.

Table IV. Atomic Coordinates (×10⁴) and Isotropic Temperature Factors (Å² × 10⁴) for Non-Hydrogen Atoms of Complex 1a

atom	*x/a*	*y/b*	*z/c*	U_{iso}
Cr(1)[a]	1977 (4)	855 (3)	1725.6 (8)	240 (4)
Cr(101)[b]	1814 (4)	1230 (4)	1749 (1)	240 (4)
N(1)[a]	1513 (14)	−930 (9)	1640 (4)	364 (16)
N(2)[a]	55 (10)	1489 (14)	1785 (4)	364 (16)
N(101)[b]	1151 (19)	−537 (11)	1690 (5)	364 (16)
N(102)[b]	−9 (12)	2071 (16)	1764 (5)	364 (16)
O(1)[a]	1248 (16)	−2209 (11)	1642 (4)	615 (20)
O(2)[a]	−1208 (13)	1991 (15)	1889 (4)	615 (20)
O(101)[b]	664 (18)	−1775 (13)	1669 (5)	615 (20)
O(102)[b]	−1226 (15)	2711 (17)	1826 (4)	615 (20)
O(3)	2254 (6)	3166 (6)	618 (1)	287 (12)
O(4)	1202 (6)	3867 (6)	1177 (1)	373 (12)
C(1)[a]	3631 (10)	158 (10)	2179 (2)	274 (9)
C(2)[a]	4591 (10)	775 (10)	1877 (2)	274 (9)
C(3)[a]	4159 (10)	2282 (10)	1838 (3)	274 (9)
C(4)[a]	2932 (10)	2588 (10)	2114 (2)	274 (9)
C(5)[a]	2618 (10)	1282 (10)	2331 (2)	274 (9)
C(11)[a]	3721 (14)	−1402 (12)	2325 (3)	514 (15)
C(12)[a]	5856 (12)	−14 (15)	1645 (3)	514 (15)
C(13)[a]	4937 (14)	3375 (15)	1567 (3)	514 (15)
C(14)[a]	2240 (13)	4091 (13)	2196 (3)	514 (15)
C(15)[a]	1501 (12)	1153 (16)	2672 (3)	514 (15)
C(101)[b]	3193 (11)	623 (11)	2279 (3)	274 (9)
C(102)[b]	4295 (11)	751 (11)	1964 (3)	274 (9)
C(103)[b]	4237 (11)	2225 (11)	1829 (3)	274 (9)
C(104)[b]	3096 (11)	2998 (11)	2056 (2)	274 (9)
C(105)[b]	2459 (11)	2011 (11)	2338 (3)	274 (9)
C(111)[b]	2913 (16)	−744 (14)	2513 (3)	514 (15)
C(112)[b]	5425 (14)	−418 (16)	1821 (4)	514 (15)
C(113)[b]	5335 (14)	2903 (18)	1532 (3)	514 (15)
C(114)[b]	2797 (15)	4626 (13)	2039 (4)	514 (15)
C(115)[b]	1279 (13)	2374 (18)	2654 (3)	514 (15)
C(6)	2357 (9)	1496 (8)	1158 (1)	295 (17)
C(7)	1939 (10)	2819 (8)	989 (2)	296 (16)
C(8)	3005 (10)	2189 (8)	373 (2)	294 (16)
C(9)	3493 (9)	866 (9)	512 (2)	320 (18)
C(10)	3116 (10)	544 (8)	909 (2)	353 (18)
C(16)	823 (11)	5264 (10)	989 (2)	505 (24)
C(17)	4394 (10)	−261 (9)	279 (2)	420 (21)
C(18)	3386 (12)	−1604 (10)	171 (3)	610 (27)
C(21)	3220 (10)	2831 (8)	−19 (2)	292 (16)
C(22)	3782 (9)	4268 (9)	−61 (2)	359 (20)
C(23)	3953 (10)	4851 (10)	−430 (2)	429 (22)
C(24)	3541 (9)	4045 (10)	−753 (2)	413 (20)
C(25)	2980 (10)	2624 (9)	−712 (2)	364 (19)
C(26)	2810 (9)	1994 (9)	−347 (2)	337 (19)

[a] Site occupancy = 0.543 (6). [b] Site occupancy = (1 − 0.543 (6)).

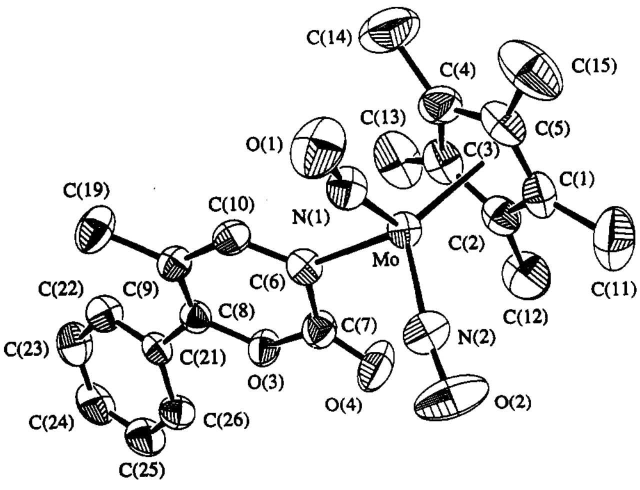


Figure 2. Solid-state molecular structure of complex **2b**, the hydrogen atoms having been omitted for clarity.

Results and Discussion

The new chemistry being reported in this note is summarized in Scheme I. Thus, as shown in the first step of this scheme, the synthesis of the 2-pyrone-containing complexes, $[\mathrm{Cp^*M(NO)_2}\overline{\mathrm{C{=}C(H)C(R){=}C(Ph)OC}}{=}\mathrm{OMe}]\mathrm{BF_4}$ ($\mathrm{Cp^*} = \eta^5\text{-}\mathrm{C_5Me_5}$; M = Cr, R = Et (**1a**); M = Mo, R = Me (**1b**); M = W, R = Me (**1c**)) results from the condensation of methyl propiolate with the appropriate

Table V. Atomic Coordinates (×10⁴) and Isotropic Temperature Factors (Å² × 10⁴) for Non-Hydrogen Atoms of Complex 2b

atom	*x/a*	*y/b*	*z/c*	U_{eq}
Mo	8072.0 (1)	7254.9 (2)	262.3 (1)	332
O(1)	6816 (1)	8023 (3)	1254 (1)	632
O(2)	8911 (2)	4702 (3)	1460 (1)	742
O(3)	7306.8 (9)	4167 (2)	−2100 (1)	397
O(4)	8497 (1)	4587 (3)	−1029 (1)	604
N(1)	7265 (1)	7582 (2)	831 (1)	421
N(2)	8537 (1)	5630 (2)	956 (1)	463
C(1)	9311 (1)	8669 (3)	629 (2)	464
C(2)	9182 (1)	8160 (3)	−283 (2)	440
C(3)	8432 (2)	8817 (3)	−833 (1)	462
C(4)	8091 (2)	9722 (3)	−267 (2)	499
C(5)	8648 (2)	9638 (3)	643 (2)	462
C(11)	10078 (2)	8290 (4)	1433 (2)	757
C(12)	9799 (2)	7233 (3)	−607 (3)	690
C(13)	8088 (2)	8679 (4)	−1867 (1)	698
C(14)	7323 (2)	10714 (4)	−579 (3)	840
C(15)	8559 (2)	10498 (4)	1466 (2)	735
C(7)	7763 (2)	4928 (3)	−1307 (2)	435
C(6)	7317 (1)	6014 (3)	−923 (1)	363
C(10)	6478 (1)	6109 (3)	−1331 (2)	377
C(9)	6013 (1)	5251 (3)	−2115 (2)	373
C(19)	5065 (2)	5408 (4)	−2439 (2)	545
C(8)	6455 (1)	4317 (3)	−2494 (1)	349
C(21)	6187 (1)	3351 (3)	−3316 (2)	354
C(22)	5471 (2)	3651 (3)	−4043 (2)	483
C(23)	5252 (2)	2711 (3)	−4808 (2)	571
C(24)	5730 (2)	1514 (3)	−4869 (2)	581
C(25)	6441 (2)	1211 (3)	−4160 (2)	591
C(26)	6669 (2)	2120 (3)	−3398 (2)	491

Table VI. Selected Bond Distances (Å) and Angles (deg) for Complex 1a

Cr–Cp[b]	1.85	Cr–C(6)	2.08
Cr–N	1.70	N–O	1.19
O(3)–C(7)	1.340 (8)	C(8)–C(9)	1.352 (10)
O(3)–C(8)	1.371 (8)	C(8)–C(21)	1.482 (9)
O(4)–C(7)	1.301 (8)	C(9)–C(10)	1.433 (9)
O(4)–C(16)	1.457 (10)	C(9)–C(17)	1.498 (10)
C(6)–C(7)	1.377 (10)	C(17)–C(18)	1.521 (12)
C(6)–C(10)	1.369 (9)		

Cp–Cr–N	121	N–Cr–N	98
Cp–Cr–C(6)	115	C(6)–Cr–N	98
C(7)–C(6)–Cr(1)	127.4 (5)	O–N–Cr	171
C(10)–C(6)–Cr(1)	119.1 (5)	C(7)–C(6)–Cr(101)	117.2 (5)
C(8)–O(3)–C(7)	121.5 (6)	C(10)–C(6)–Cr(101)	129.3 (5)
C(10)–C(6)–C(7)	113.5 (5)	C(16)–O(4)–C(7)	120.9 (6)
O(4)–C(7)–O(3)	113.2 (6)	C(21)–C(8)–C(9)	129.3 (7)
C(6)–C(7)–O(3)	124.0 (6)	C(10)–C(9)–C(8)	116.9 (7)
C(6)–C(7)–O(4)	122.8 (6)	C(17)–C(9)–C(8)	124.4 (6)
C(9)–C(8)–O(3)	119.4 (6)	C(17)–C(9)–C(10)	118.8 (7)
C(21)–C(8)–O(3)	111.2 (6)	C(9)–C(10)–C(6)	124.7 (7)
C(22)–C(21)–C(8)	120.1 (7)	C(18)–C(17)–C(9)	113.8 (7)
C(26)–C(21)–C(8)	119.6 (6)		

[a] Average values are given for the disordered Cp*Cr(NO)₂ fragment. [b] Cp represents the center of mass of the ring carbon atoms of the pentamethylcyclopentadienyl ligand.

Table VII. Selected Bond Distances (Å) and Angles (deg) for Complex 2b

		corrected[a]			corrected[a]
Mo–N(1)	1.818 (2)	1.826[b]	Mo–C(1)	2.336 (2)	2.341
Mo–N(2)	1.828 (2)	1.841[b]	Mo–C(2)	2.372 (2)	2.377
Mo–Cp*[c]	2.03		Mo–C(3)	2.381 (2)	2.386
Mo–C(6)	2.174 (2)	2.176	Mo–C(4)	2.351 (2)	2.356
O(1)–N(1)	1.185 (3)	1.224[b]	Mo–C(5)	2.336 (2)	2.341
O(2)–N(2)	1.175 (3)	1.234[b]	C(7)–C(6)	1.444 (3)	1.451
O(3)–C(7)	1.398 (3)	1.400	C(6)–C(10)	1.349 (3)	1.356
O(3)–C(8)	1.369 (3)	1.377	C(10)–C(9)	1.438 (3)	1.439
O(4)–C(7)	1.205 (3)	1.212	C(9)–C(19)	1.509 (3)	1.517
C(8)–C(21)	1.476 (3)	1.478	C(9)–C(8)	1.348 (3)	1.355
C(1)–C(2)	1.417 (3)	1.427	C(1)–C(11)	1.521 (1)	1.534
C(1)–C(5)	1.405 (3)	1.416	C(2)–C(12)	1.506 (1)	1.518
C(2)–C(3)	1.408 (3)	1.420	C(3)–C(13)	1.513 (1)	1.524
C(3)–C(4)	1.415 (4)	1.426	C(4)–C(14)	1.509 (1)	1.522
C(4)–C(5)	1.423 (4)	1.434	C(5)–C(15)	1.514 (1)	1.524
C(21)–C(22)	1.390 (3)	1.396	C(23)–C(24)	1.352 (4)	1.360
C(21)–C(26)	1.387 (3)	1.395	C(24)–C(25)	1.371 (4)	1.377
C(22)–C(23)	1.395 (4)	1.396	C(25)–C(26)	1.375 (4)	1.376

N(2)–Mo–N(1)	95.60 (9)	Cp–Mo–N(1)	119.87
C(6)–Mo–N(1)	98.73 (9)	Cp–Mo–N(2)	124.94
C(6)–Mo–N(2)	96.69 (9)	Cp–Mo–C(6)	115.58
O(1)–N(1)–Mo	168.3 (2)	C(8)–O(3)–C(7)	123.9 (2)
O(2)–N(2)–Mo	171.9 (2)	C(9)–C(8)–O(3)	119.6 (2)
C(7)–C(6)–Mo	116.1 (2)	C(21)–C(8)–O(3)	109.2 (2)
C(10)–C(6)–Mo	127.9 (2)	C(21)–C(8)–C(9)	131.2 (2)
C(10)–C(6)–C(7)	115.9 (2)	C(19)–C(9)–C(10)	118.4 (2)
O(4)–C(7)–O(3)	114.5 (2)	C(8)–C(9)–C(10)	117.3 (2)
C(6)–C(7)–O(3)	117.7 (2)	C(8)–C(9)–C(19)	124.3 (2)
C(6)–C(7)–O(4)	127.8 (2)	C(9)–C(10)–C(6)	125.4 (2)
C(22)–C(21)–C(8)	122.4 (2)	C(23)–C(22)–C(21)	120.1 (3)
C(26)–C(21)–C(8)	120.2 (2)	C(24)–C(23)–C(22)	121.3 (3)
C(26)–C(21)–C(22)	117.4 (2)	C(25)–C(24)–C(23)	119.3 (3)
C(5)–C(1)–C(2)	108.6 (2)	C(26)–C(25)–C(24)	120.4 (3)
C(11)–C(1)–C(2)	124.5 (3)	C(25)–C(26)–C(21)	121.5 (3)
C(11)–C(1)–C(5)	126.7 (3)	C(5)–C(4)–C(3)	107.5 (2)
C(3)–C(2)–C(1)	107.5 (2)	C(14)–C(4)–C(3)	126.5 (3)
C(12)–C(2)–C(1)	125.1 (3)	C(14)–C(4)–C(5)	125.7 (3)
C(12)–C(2)–C(3)	127.0 (3)	C(4)–C(5)–C(1)	107.8 (2)
C(4)–C(3)–C(2)	108.5 (2)	C(15)–C(5)–C(1)	126.3 (3)
C(13)–C(3)–C(2)	125.6 (3)	C(15)–C(5)–C(4)	125.8 (3)
C(13)–C(3)–C(4)	125.7 (3)		

[a] Bond lengths based on a segmented rigid body analysis of the anisotropic thermal parameters (see text). [b] A riding correction was included for the Mo–N and N–O bond lengths. [c] Cp* represents the center of mass of the five atoms C(1)–C(5).

acetylenes. This condensation is mediated by the formally 16-electron cations[15,22] $[Cp^*M(NO)_2]^+$ and occurs in a regioselective manner in the coordination sphere of the metal. This regioselectivity is indicated by the fact that NMR spectra of crude samples of complexes 1 indicate the presence of just one isomer in solution. The cations **1a–c** may be subsequently O-demethylated (as depicted in step two of Scheme I) to obtain the neutral compounds, $Cp^*M(NO)_2\overline{C{=}C(H)C(R){=}C(Ph)OC}{=}O$ (M = Cr, R = Et (**2a**); M = Mo, R = Me (**2b**); M = W, R = Me (**2c**)). X-ray crystallographic analyses of compounds **1a** and **2b** confirm that the pyrone groups are indeed formed in a regioselective manner, with only the 5-alkyl-6-phenyl isomer being isolated in both cases. Finally, as shown in step three of Scheme I, the reaction of complexes **2a–c** with I_2 yields $Cp^*M(NO)_2I$ and the free iodopyrones, $I\overline{C{=}C(H)C(R){=}C(Ph)OC}{=}O$ (R = Et (**3a**), Me (**3b**)). The recovered $Cp^*M(NO)_2I$ may be treated with $AgBF_4$ to regenerate the organometallic cations required as reagents in the first step. Thus, the overall result of the transformations shown in Scheme I is a four-step stoichiometric cycle constituting the assembly of a functionalized 2-pyrone from readily available components, from which the recovered organometallic complex may be isolated and reused. To our knowledge, this constitutes the first reported synthesis of a 2-pyrone via the reaction of an acetylene with an acetylene ester.

The solid-state molecular structures of complexes **1a** and **2b** have been determined as representative examples of the cationic and neutral pyrone-containing complexes, respectively, and are shown in Figures 1 and 2. The intramolecular dimensions of **1a** and **2b** (Tables VI and VII) are comparable to those exhibited by related three-legged piano-stool organometallic complexes possessing essentially linear M–N–O groups and normal M–C(6) bonds.[23] In

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(22) This reactivity is a logical extension of a lactone synthesis previously developed in these laboratories; see: Legzdins, P.; Richter-Addo, G. B.; Einstein, F. W. B.; Jones, R. H. *Organometallics* **1990**, *9*, 432.

(23) For examples see ref 22 and references cited therein.

both **1a** and **2b** the pyrone ring is planar or very nearly so. However, the bond lengths and bond angles in the 2-pyrone rings of **1a**, as compared to those in **2b**, are reflective of a significant delocalization of π-electron density over the metal-attached C–CO_2 fragments. This feature is indicated by the shorter C(7)–C(6) and C(7)–O(3) bonds and longer C(7)–O(4) bond in complex **1a**. This delocalization is probably a manifestation of the positive charge extant in the pyrone ring and is similar in magnitude to that exhibited by the related lactone complexes.[22] The key information gained in each case is that the crystallographic analyses of **1a** and **2b** confirm the existence of the isolated pyrone complex as only one of two possible regioisomers with respect to the formation of the pyrone ring (vide supra). This regioselectivity is important synthetically since it allows for selective functionalization of the 5- and 6-positions of the 2-pyrone moiety.

The analytical and spectroscopic data for all isolated pyrone complexes are collected in Tables I and II. The salts **1a–c** are green, air-stable solids which are soluble in polar solvents such as THF, CH_2Cl_2, and acetone. The neutral complexes **2a–c**, on the other hand, are brown, air-stable solids which display the expected solubility in less polar solvents such as Et_2O and benzene. The spectroscopic properties of complexes **1a–c** and **2a–c** are unremarkable and are fully consistent with the complexes possessing molecular structures similar to those established crystallographically for **1a** and **2b** and retaining these structures in solutions.

The generality of the reactions outlined in Scheme I remains to be established. For example, it may be feasible to incorporate other heteroatoms into the organic ring, with lactams and thiolactones being possible products. It should be possible to extend the condensations effected by the $[Cp^*M(NO)_2]^+$ cations to encompass acetylene esters other than methyl propiolate and to effect the removal of the assembled 2-pyrone from the metal center with a variety of reagents (e.g. HCl, Me_3SiCl, etc.). Also feasible is the insertion of electrophiles of the type NE^+ (E = O, p-$O_2NC_6H_4N$, S) into the Cr–C bond of complex **2a** or its analogues, since such insertions into Cr–C σ bonds have precedent in these systems.[24] It remains to be seen if the selectivity of formation of the pyrone ring can be maintained without the presence of a phenyl group, but if so, this could allow for the formation of 2-pyrone molecules with selective functionalization of the pyrone ring at all four available ring positions. At present, no known synthetic route leading to 2-pyrones allows for such selective substitution.[6a]

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Registry No. **1a**, 141526-55-8; **1b**, 141508-00-1; **1c**, 141508-02-3; **2a**, 141508-03-4; **2b**, 141508-04-5; **2c**, 141508-05-6; **3a**, 141507-97-3; **3b**, 141507-98-4; $[Cp^*Cr(NO)_2]BF_4$, 124921-16-0; $[Cp^*Mo(NO)_2]BF_4$, 124921-20-6; $[Cp^*W(NO)_2]BF_4$, 124921-24-0; $Cp^*Cr(NO)_2Cl$, 110681-76-0; HC≡CCO_2Me, 922-67-8; EtC≡CPh, 622-76-4; MeC≡CPh, 673-32-5; I_2, 7553-56-2.

Supplementary Material Available: Tables of fractional atomic coordinates and isotropic temperature factors for the remaining atoms and remaining bond distances and angles for $[Cp^*Cr(NO)_2\overline{C{=}C(H)C(Et){=}C(Ph)OC}{=}OMe]BF_4$ (**1a**) and torsion angles, H atom coordinates and isotropic temperature factors, and anisotropic thermal parameters for $Cp^*Mo(NO)_2\overline{C{=}C(H)C(Me){=}C(Ph)OC}{=}O$ (**2b**) (9 pages). Ordering information is given on any current masthead page.

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A Silyl Carborane Containing the *closo*-1,10-$C_2B_8H_8$ Fragment

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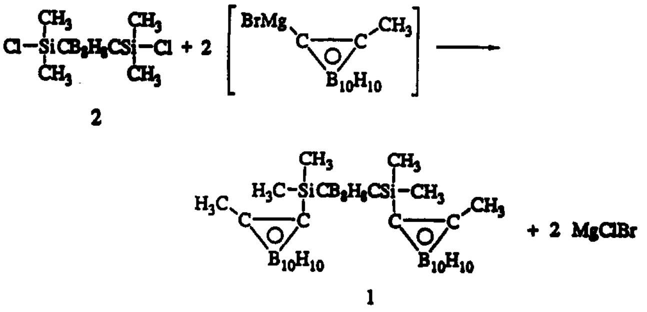
Summary: When 1,10-$(Si(CH_3)_2Cl)_2$-*closo*-1,10-$C_2B_8H_8$ was reacted with 2 equiv of 1-CH_3-2-MgBr-*closo*-1,2-$C_2B_{10}H_{10}$, 1,10-(1′-$Si(CH_3)_2$-2′-CH_3-*closo*-1′,2′-$C_2B_{10}H_{10})_2$-*closo*-1,10-$C_2B_8H_8$ (**1**) was isolated in 51% yield. The molecular structure of **1** was determined by single-crystal X-ray diffraction techniques. Compound **1** crystallized in the monoclinic space group $P2_1/c$: a = 13.1739 (9), b = 7.2412 (5), and c = 18.886 (1) Å; β = 107.905 (2)°; V = 1714 Å^3; and Z = 2 (two centrosymmetric molecules, achieved by disordering the C_2B_8 moiety). Data were collected on a Huber diffractometer constructed at UCLA, using Mo Kα radiation, to a maximum 2θ = 50°, giving 3028 unique reflections. The structure was solved by direct methods (SHELX86). The final discrepancy index was R = 0.074, R_w = 0.097 for 2022 independent reflections with $I > 3\sigma(I)$.

Scheme I



Silyl derivatives of the isomers of *closo*-$C_2B_{10}H_{12}$ have been known since the 1960s.[1–4] However, although a large

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