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A New Carborane–Ylide Reaction. Synthesis and Structural Characterization of a Seven-Vertex *nido*-Carborane Zwitterion: *exo*-6-(Me_3P^+–CH_2)-3,4-Et_2-*nido*-3,4-$C_2B_5H_5^-$

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Summary: The carborane, *closo*-2,3-$Et_2C_2B_5H_5$ readily reacts with the phosphorus ylide, trimethylmethylenephosphorane to give the seven-vertex, *nido*-carborane zwitterion, *exo*-6-($Me_3P^+CH_2$)-3,4-Et_2-*nido*-3,4-$C_2B_5H_5^-$. The structure of this compound was established by a single-crystal X-ray study which showed that, consistent with its 18-skeletal-electron count, the carborane has a cage framework that can be derived from a closo-dodecahedral polyhedron by removal of one five-coordinate vertex. The ylide group is bonded to the B6 boron of the cage and is considered a two-electron donor to the cage framework. The bond distances and angles in the ylide substituent indicate a reduction in the phosphorus–carbon bond order in comparison to the free ylide. Thus, the compound should be viewed as a zwitterion containing a phosphonium center linked to the anionic carborane cage by a phosphorus–boron bridging methylene.

The reactions of phosphorus ylides with boron compounds have been observed to result in the formation of dipolar adducts or, if acidic hydrogens are present, phosphonium salts.[1]

$$2R_3P{=}CH_2 + B_2H_6 \rightarrow 2R_3P^+\text{-}CH_2\text{-}BH_3^- \quad (1)$$

$$R_3P{=}CH_2 + B_{10}H_{14} \rightarrow R_3PCH_3^+B_{10}H_{13}^- \quad (2)$$

In this note, we report a new type of reaction between an ylide and a closo-polyhedral borane which results in both adduct formation and cage opening to produce the corresponding zwitterionic nido cage system. As an illustration, the synthesis and structural characterization of the new seven-vertex *nido*-carborane zwitterion *exo*-6-(Me_3P^+–CH_2)-3,4-Et_2-*nido*-3,4-$C_2B_5H_5^-$, which is obtained by the reaction of *closo*-2,3-$Et_2C_2B_5H_5$ carborane with trimethylmethylenephosphorane, is presented.

Experimental Section

All manipulations were carried out by using standard high-vacuum or inert-atmosphere techniques as described by Shriver.[2]

Materials. The compounds *closo*-2,3-$Et_2C_2B_5H_5$[3] and trimethylmethylenephosphorane[4] were prepared according to the literature methods. The trimethylmethylenephosphorane was stored at 0 °C as a glyme solution until use. Benzene and glyme were dried over sodium benzophenone and freshly distilled before use. Hexane was purchased from Aldrich and used as received.

Physical Measurements. ^{11}B NMR spectra at 64.2 MHz, ^{13}C NMR spectra at 50.3 MHz, and ^{31}P NMR spectra at 81.0 MHz were obtained on a Bruker AF-200 spectrometer equipped with the appropriate decoupling accessories. Proton NMR spectra at 500 MHz and ^{13}C NMR spectra at 125.7 MHz were obtained on a Bruker AM-500 spectrometer. All ^{11}B chemical shifts were referenced to external $BF_3{\cdot}O(C_2H_5)_2$ (0.0 ppm), with a negative sign indicating an upfield shift. All proton and carbon chemical shifts were measured relative to internal residual protons or carbons from the lock solvents and then referenced to Me_4Si (0.0 ppm). The ^{31}P chemical shift was measured relative to external 85% H_3PO_4, with a positive sign indicating a low-field shift. The high-resolution mass spectrum was obtained on a VG Micromass 7070H mass spectrometer. The infrared spectrum was obtained on a Perkin–Elmer 7770 Fourier transform spectrometer. Microanalysis was performed at Robertson Microlit, Madison, NJ.

Table I. Crystallographic Data for *exo*-6-(Me_3P^+–CH_2)-3,4-Et_2-*nido*-3,4-$C_2B_5H_5^-$

formula	$C_{10}H_{26}PB_5$
fw	231.35
cryst class	orthorhombic
space group	*Pbca* (No. 61)
Z	16
cell constants	
a, Å	38.539 (5)
b, Å	12.949 (2)
c, Å	12.804 (2)
V, Å^3	6390 (3)
cryst size, mm	0.05 × 0.08 × 0.38
μ, cm^{-1}	12.58
D_{calc}, g/cm^3	0.962
$F(000)$	2016
radiation (λ, Å)	Cu Kα (1.541 84)
θ range, deg	2.0–45.0
scan mode	ω–2θ
hkl collcd	+35,+11,+11
no. of reflns measd	2978
no. of unique reflns	2579
no. of reflns ($F^2 > 3.0\sigma$)	1456
no. of params	298
data/param ratio	4.9
R_1	0.082
R_2	0.098
GOF	2.149

Synthesis of *exo*-6-(Me_3P^+–CH_2)-3,4-Et_2-*nido*-3,4-$C_2B_5H_5^-$. A 0.12 g (0.85-mmol) sample of *closo*-2,3-$Et_2C_2B_5H_5$ and 20 mL of benzene were condensed into a 100-mL two-neck flask equipped with a vacuum stopcock. The solution was then warmed to room temperature and purged with N_2, and 7.5 mL (0.12 mmol/mL) of $CH_2{=}PMe_3$ solution in glyme was added dropwise by syringe over 5 min. The flask was then allowed to stir at room temperature for 1 h. ^{11}B NMR spectra taken at this point showed quantitative conversion to the final product. Subsequent vacuum evaporation of the solvent and unreacted ylide gave 0.19 g (0.82 mmol, 96.5% yield) of crude white product. Recrystallization from benzene/hexane afforded 0.15 g of pure crystalline *exo*-6-(Me_3P^+–CH_2)-3,4-Et_2-*nido*-3,4-$C_2B_5H_5^-$. Anal. Calc: C, 51.86; H, 11.23. Found: C, 51.46; H, 11.23. Exact mass calcd for $^{11}B_5{}^{12}C_{10}{}^{31}P^1H_{26}$: 232.2337. Found: 232.2272. Mp: 142 °C dec. FTIR (KBr, cm^{-1}): 2978 (vs), 2964 (vs), 2921 (vs), 2865 (s), 2524 (vs), 2482 (vs), 2255 (w), 2184 (w), 2070 (w), 1950 (w), 1592 (w), 1457 (m), 1421 (s), 1372 (m), 1315 (m), 1301 (m), 1258 (m), 1180 (m), 1095 (m), 1067 (m), 1038 (m), 982 (m), 953 (m), 889 (m), 811 (m), 769 (w), 726 (w), 648 (w). ^{11}B NMR [CD_2Cl_2, ppm (J, Hz)]: δ 18.5 (d, B2, J_{BH} 139), 11.3 (d, B6, J_{BH} 111), 0.2 (d, B5,7, J_{BH} 122), −26.0 (d, B1, J_{BH} 156). 2D ^{11}B–^{11}B NMR established the following connectivities: B1–B2; B2–B6; B2–B5,7; B6–B5,7 (weak). ^{13}C NMR (25 °C, 125.7 MHz, CD_2Cl_2, ppm): δ ~135 (br, cage carbons), 24.5 (s, CH_2), ~19 (br, P–CH_2), 15.4 (s, CH_3), 11.0 (d,

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[1] See, for example: (a) Hawthorne, M. F. *J. Am. Chem. Soc.* **1958**, *80*, 3480–3481. (b) Seyferth, D.; Grim, S. O. *J. Am. Chem. Soc.* **1961**, *83*, 1613–1616. (c) Hawthorne, M. F. *J. Am. Chem. Soc.* **1961**, *83*, 367–369.

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P–CH_3, J_{CP} 55.2). ^{13}C NMR (−85 °C, 50.3 MHz, CD_2Cl_2, ppm): δ 135.2 (s, cage carbons), 23.7 (s, CH_2), 17.7 (d, CH_2, J_{CP} 34.1), 15.0 (s, CH_3), 10.0 (d, P–CH_3, J_{CP} 55.5). ^1H NMR (CD_2Cl_2, ppm): δ 2.34 (m, 4 H, CH_2), 1.67 (d, J_{PH} 13.6, 9 H, CH_3), 1.44 (d of d, J_{PH} 17.5, J_{HH} 7, 2 H, CH_2), 1.14 (t, 6 H, CH_3). ^{31}P NMR (CD_2Cl_2, ppm): δ 24.3 (s).

Crystallographic Data for *exo*-6-(Me_3P^+–CH_2)-3,4-Et_2-*nido*-3,4-$C_2B_5H_5^-$. Single crystals of *exo*-6-(Me_3P^+–CH_2)-3,4-Et_2-*nido*-3,4-$C_2B_5H_5^-$ were grown by slow evaporation of a benzene/heptane solution under argon. A suitably sized crystal was placed inside a capillary tube, which was then sealed with glue and mounted on the diffractometer. Refined cell dimensions and their standard deviations were obtained from least-squares refinement of 25 accurately centered reflections.

Collection and Reduction of the Data. Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer employing graphite-monochromated Cu Kα radiation and using the ω–2θ scan technique. Three standard reflections measured every 3500 s of X-ray exposure showed no intensity decay over the course of data collection. The intensity data were corrected for Lorentz and polarization effects, but not for absorption.

Solution and Refinement of the Structure. All calculations were performed on a VAX 11/750 computer using the Enraf-Nonius structure package. The full-matrix least-squares refinement was phased on F, and the function minimized was $\sum w(|F_o| |F_c|)^2$. The weights (w) were taken as $4F_o^2/(\sigma(F_o^2))^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The neutral-atom scattering factors and complex anomalous dispersion corrections are those stored in the SDP package. Agreement factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum(|F_o| - |F_c|)^2/\sum|F_o|^2)^{1/2}$.

The structure was solved by direct methods (MULTAN 11/82). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included as constant contributions to the structure factors and were not refined. Large thermal motions were observed for all ethyl fragments and for the methyl C32 carbon in particular, indicating disorder. Therefore, a disorder model was used consisting of two C32 positions each with 0.5 populations.

Table II. Refined Positional Parameters for *exo*-6-($Me_3P^+CH_2$)-3,4-Et_2-*nido*-3,4-$C_2B_5H_5^-$

atom	x	y	z	B_{eq},[a] Å^2
P	0.73638 (8)	0.2020 (2)	0.5210 (3)	7.05 (8)
B1	0.6841 (4)	−0.020 (1)	0.189 (1)	8.6 (4)
B2	0.7179 (3)	0.037 (1)	0.250 (1)	6.4 (4)
B5	0.7067 (3)	−0.084 (1)	0.300 (1)	6.4 (4)
B6	0.7120 (3)	0.051 (1)	0.381 (1)	6.1 (3)
B7	0.6793 (4)	0.097 (1)	0.270 (1)	8.2 (4)
C3	0.6519 (3)	0.0116 (9)	0.280 (1)	8.6 (4)
C4	0.6667 (3)	−0.0851 (9)	0.2962 (9)	8.2 (3)
C31	0.6121 (3)	0.027 (1)	0.262 (2)	13.9 (6)
C32(1)	0.6021 (9)	0.089 (3)	0.189 (3)	16 (1)
C32(2)	0.5940 (7)	0.101 (2)	0.291 (3)	13 (1)
C41	0.6419 (4)	−0.200 (2)	0.263 (2)	19.5 (8)
C42	0.6418 (4)	−0.212 (1)	0.360 (2)	21.4 (8)
C61	0.7459 (3)	0.1034 (9)	0.4310 (8)	7.5 (3)
C62	0.7753 (3)	0.267 (1)	0.5652 (9)	8.6 (4)
C63	0.7093 (3)	0.2959 (9)	0.463 (1)	8.9 (3)
C64	0.7145 (3)	0.150 (1)	0.6314 (8)	8.0 (3)
P′	0.48235 (7)	0.2566 (2)	0.0380 (2)	5.67 (7)
B1′	0.4411 (3)	−0.108 (1)	0.234 (1)	6.8 (4)
B2′	0.4739 (3)	−0.030 (1)	0.193 (1)	6.3 (4)
B5′	0.4529 (3)	0.010 (1)	0.304 (1)	6.4 (4)
B6′	0.4601 (4)	0.094 (1)	0.170 (1)	6.4 (4)
B7′	0.4391 (4)	−0.033 (1)	0.113 (1)	6.9 (4)
C3′	0.4072 (3)	−0.0405 (8)	0.1813 (9)	6.8 (3)
C4′	0.4148 (2)	−0.0164 (7)	0.2877 (9)	6.6 (3)
C31′	0.3720 (3)	−0.087 (1)	0.151 (1)	12.3 (5)
C32′	0.3493 (4)	−0.001 (1)	0.124 (2)	19.0 (7)
C41′	0.3884 (4)	−0.061 (2)	0.393 (2)	23.1 (7)
C42′	0.3771 (4)	0.027 (2)	0.395 (1)	22.8 (6)
C61′	0.4947 (2)	0.1589 (8)	0.1279 (9)	6.7 (3)
C62′	0.5192 (3)	0.3066 (8)	−0.0276 (9)	7.4 (3)
C63′	0.4612 (3)	0.3595 (8)	0.1056 (8)	6.5 (3)
C64′	0.4525 (3)	0.2081 (8)	−0.0580 (8)	7.4 (3)

[a] $B_{eq} = {}^4/_3[\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab \cos\gamma + \beta_{13}ac \cos\beta + \beta_{23}bc \cos\alpha]$.

Results and Discussion

The carbon–phosphorus bond in trimethylmethylenephosphorane is highly polarized, with the carbon atom having a partial negative charge.[5] Thus, the ylide can function as a strong nucleophile. We have previously demonstrated that *closo*-2,3-$Et_2C_2B_5H_5$ undergoes a cage-opening rearrangement upon reaction with other nucleophiles, including hydride and trimethylphosphine.[3] Likewise, Onak has reported[6] that another small carborane, *closo*-2,4-$C_2B_4H_6$, forms, upon treatment with either trimethylamine or trimethylphosphine, open-cage dipolar adducts, such as 5-$(CH_3)_3N^+$-2,4-$C_2B_4H_6^-$. These previous results suggested that *closo*-2,3-$Et_2C_2B_5H_5$ should also form an open-cage zwitterionic adduct upon reaction with trimethylmethylenephosphorane and, furthermore, that such a species might then give rise to carbon-inserted products, for example *arachno*-Me_3P-$Et_2C_3B_5H_7$ or *nido*-$Et_2C_3B_5H_7$.

The carborane *closo*-2,3-$Et_2C_2B_5H_5$ was found to react cleanly with trimethylmethylenephosphorane in benzene solvent to give *exo*-6-(Me_3P^+–CH_2)-3,4-Et_2-*nido*-3,4-$C_2B_5H_5^-$ as the only product.

$$\textit{closo}\text{-2,3-}Et_2C_2B_5H_5 + CH_2{=}PMe_2 \rightarrow \textit{exo}\text{-6-}(Me_3P^+\text{–}CH_2)\text{-3,4-}Et_2\text{-}\textit{nido}\text{-3,4-}C_2B_5H_5^- \quad (3)$$

The product is air stable and soluble in benzene and ethers but insoluble in hydrocarbons. The ^{11}B NMR spectrum (Figure 1) consists of four doublets in a 1:1:2:1 ratio, at shifts similar to those observed for the isoelectronic anion *nido*-3,4-$Et_2C_2B_5H_6^-$ [7] and the trimethylphosphine adduct *nido*-6-Me_3P^+-3,4-$Et_2C_2B_5H_5^-$,[3b] suggesting that these compounds have similar cage frameworks. The assignments given in the figure are further consistent with the connectivities observed in the 2D ^{11}B–^{11}B NMR spectrum of the compound. The ^1H NMR spectrum shows, in addition to the cage ethyl and phosphine methyl resonances, a doublet of doublets resonance of intensity 2 at 1.44 ppm that is assigned to the hydrogens on the bridging methylene group which are coupled to both the phosphorus and to the proton on the B6 cage boron. The room-temperature proton-decoupled ^{13}C NMR spectrum shows the expected resonances for the cage ethyl group and a doublet resonance for the methyl carbons attached to the phosphorus; however, the bridging methylene carbon resonance, because of its coupling with the B6 boron, was too broad to be conclusively identified. However, when the ^{13}C NMR spectrum was recorded at −85 °C, the boron–carbon-13 interaction was thermally decoupled,[8] and a doublet resonance was clearly observed. The chemical shift (17.7 ppm) and coupling constant (J_{CP} 34 Hz) observed for this resonance are in the ranges observed for phosphonium carbons.[9] Likewise the observed

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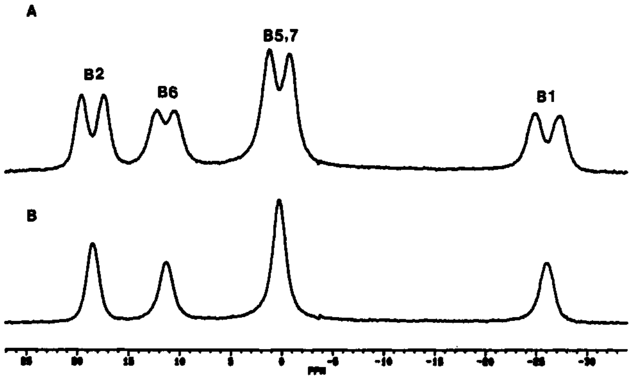

Figure 1. 64.2-MHz ^{11}B NMR spectra of *exo*-6-(Me_3P^+–CH_2)-3,4-Et_2-*nido*-3,4-$C_2B_5H_5^-$: (A) proton coupled; (B) proton-spin decoupled.

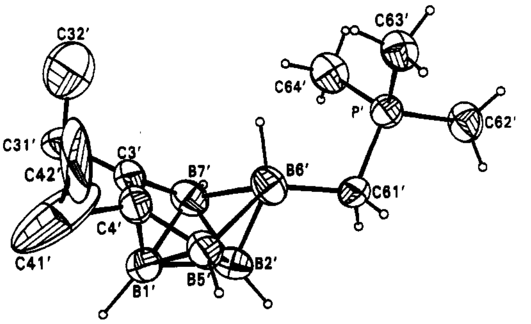

Figure 2. ORTEP drawing of the molecular structure of *exo*-6-(Me_3P^+–CH_2)-3,4-Et_2-*nido*-3,4-$C_2B_5H_5^-$. Selected bond distances (Å) and angles (deg): P′–C61′, 1.776 (11); B1′–B2′, 1.709 (18); B1′–B5′, 1.830 (18); B1′–B7′, 1.837 (19); B1′–C3′, 1.716 (16); B1′–C4′, 1.707 (16); B2′–B5′, 1.717 (18); B2′–B6′, 1.709 (18); B2′–B7′, 1.689 (18); B5′–B6′, 2.046 (18); B5′–C4′, 1.523 (16); B6′–B7′, 1.973 (18); B6′–C61′, 1.669 (16); B7′–C3′, 1.515 (17); C3′–C4′, 1.427 (16); C3′–C31′, 1.531 (16); C4′–C41′, 1.779 (23); C31′–C32′, 1.452 (21); C41′–C42′, 1.222 (29); B6′–C61′–P′, 110.9 (7); C4′–C3′–B7′, 111.9 (9); C3′–B7′–B6′, 99.7 (9); B7′–B6′–B5′, 79.3 (7); B6′–B5′–C4′, 97.8 (9); B5′–C4′–C3′, 112.2 (9).

^{31}P shift is in the phosphonium region.[10]

A single-crystal X-ray determination confirmed the structure shown in the ORTEP drawing in Figure 2. There are two independent molecules in the asymmetric unit cell, but since there are no significant differences between the two molecules in either their cage structures or intracage distances and angles, only one of these is shown in the figure. The two molecules apparently differ only with respect to the orientation of the cage ethyl groups.

The compound can be viewed as a zwitterion, with the ylide functioning as a two-skeletal-electron donor to the cage framework. This interaction then gives rise to a seven-vertex 18-skeletal-electron cluster which, on the basis of simple skeletal-electron-counting rules,[11] should adopt a nido-type cage structure based on a dodecahedron (bis(disphenoid)) missing one high-coordinate vertex. Such a cage geometry has previously been crystallographically confirmed for the *nido*-3,4-$Et_2C_2B_5H_6^-$ anion.[3b,6] The structure of *exo*-6-(Me_3P^+–CH_2)-3,4-Et_2-*nido*-3,4-$C_2B_5H_5^-$ shown in the figure is clearly consistent with the predicted cage geometry and is isostructural with that observed for *nido*-3,4-$Et_2C_2B_5H_6^-$.

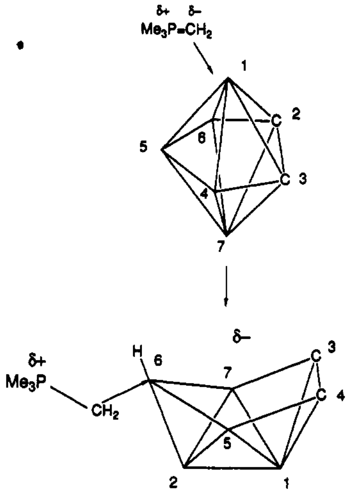

Figure 3. Possible reaction sequence leading to the formation of *exo*-6-(Me_3P^+–CH_2)-3,4-Et_2-*nido*-3,4-$C_2B_5H_5^-$.

The bond lengths and angles within the cage are similar to those observed in *nido*-3,4-$Et_2C_2B_5H_6^-$. The distances B5′–B6′ and B6′–B7′ are unusually long, 2.046 (18) and 1.973 (18) Å, respectively, suggesting weak interactions between these atoms. The remaining intracage distances and angles are within normal ranges.

The P′–C61′ bond distance, 1.776 (11) Å, is elongated in comparison to the 1.640 (6) Å value observed[12] for the phosphorus–carbon double bond in the parent trimethylmethylenephosphorane, consistent with a reduction of the bond order upon coordination to the carborane cage. This distance, the C61′–B6′ bond distance 1.669 (16) Å, and the P′–C61′–B6′ angle 110.9 (7)° are similar to those observed in $(CH_3)_3P^+$–CH_2-BH_3^-.[13] The Me–P–Me angles at the phosphorus (average 108.3°) are consistent with its tetrahedral phosphonium formulation.

Population analysis calculations[14] on the parent *closo*-2,3-$C_2B_5H_7$ indicate that the equatorial borons have the highest electron densities, while the apical borons are positively charged. Therefore, nucleophilic attacks should be directed toward the apical positions in the carborane. The final products obtained upon reaction of *closo*-2,3-$Et_2C_2B_5H_5$ with hydride,[3,6] trimethylphosphine,[3] or trimethylmethylenephosphorane are each open-cage clusters in which the incoming nucleophile is bound at the 6-boron position across from the two cage carbons. This suggests a common reaction pathway, diagrammed for the ylide reaction in Figure 3, involving initial attack of the ylide at one of the apical borons in *closo*-2,3-$Et_2C_2B_5H_5$ followed by an elongation of the carbon to apical-boron cage distances to yield the observed five-membered open face.

No evidence was observed for any carbon-inserted products in the original reaction. Likewise, thermolysis of *exo*-6-(Me_3P^+–CH_2)-3,4-Et_2-*nido*-3,4-$C_2B_5H_5^-$ resulted in only decomposition. The absence of insertion products may be a consequence of both a strong phosphorus–carbon bonding interaction and the fact that the Me_3PCH_2 group is substituted at the 6-boron in the exo-position oriented

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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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