$J = 9.9$ and 9.6 Hz, H-2 and H-6), 4.7–5.3 (2 H, two overlapping pairs of triplets, $J = 9.6$ and 9.9, $J' = 6.8$ Hz, H-3 and H-5), 5.97 (2 H, s, $-\mathrm{OCH_2}$), 7.66 (2 H, t, $J = 6.8$ Hz, H-4 and H-4′), and 8.87 (6 H, s, $-\mathrm{C(CH_3)_2}$); $\mathrm{uv}_{\max}^{\mathrm{CH_3OH}}$ 280 nm (ϵ 3100); mass spectral parent ion at *m/e* 162 (37) and fragment ions at 147 (79), 119 (40), 107 (52), 91 (42), 78 (100), and 69 (45). Irradiation of the τ 7.66 triplet in the nmr spectrum causes collapse of the two pairs of triplets at 4.7–5.3, leaving two doublets at 4.69 and 4.92, $J = 9.6$ and 9.9 Hz, respectively. The tropone–diphenylketene adduct undergoes a similar rearrangement to a product whose nmr spectrum quite closely resembles that of **4**, and to which an analogous structure was assigned on the basis of spectral and chemical evidence.[6] Compound **6**, not obtained pure, showed nmr signals at 4.1–4.3 and 4.8–5.0 (4 H, m), 5.96 (2 H, s), 7.28 (2 H, d, $J = 6.1$ Hz), and 8.95 (6 H, s), and $\nu_{\max}^{\mathrm{film}}$ 1636 and 1056 cm^{-1}. The position of the methylene group is assigned as depicted above on the basis of relative thermodynamic stabilities of substituted cycloheptatrienes; see ref 1b, footnotes 10 and 11.

Hydrogenation of **2** and of **4** over palladium/charcoal led to the uptake, in both cases, of ~98% of 3 mol of hydrogen and to the isolation of the same saturated bicyclic ether **7**: $\mathrm{ir}_{\max}^{\mathrm{film}}$ 1055 and 1080 (s) cm^{-1}; nmr ($\mathrm{CCl_4}$) τ 5.98 (1 H, m, H-1), 6.60 (2 H, AB, $\Delta\nu_{\mathrm{AB}} = 12.5$, $J = 8.1$ Hz, $-\mathrm{OCH_2}-$), 7.6–8.8 (11 H, m), and 9.06 and 9.12 (3 H each, s, $-\mathrm{C(CH_3)_2}-$); parent ion *m/e* 168*. Both **2** and **4** were unreactive to *N*-phenylmaleimide and tetracyanoethylene at 25–50°; heating **4** with an excess of either reagent at 100° led only to gums and recovered dienophile.

In similar fashion, irradiation of tropone in excess tetramethylethylene gave 40–45% of adduct **3**, bp 56–57° (0.2 mm). Compound **3** showed $\mathrm{ir}_{\max}^{\mathrm{film}}$ 1636 and 1070 cm^{-1}; nmr ($\mathrm{CCl_4}$) τ 3.78 (2 H, m), 4.30 (2 H, m), 4.79 (1 H, 2 d, $J = 9.3$, $J' = 2.9$ Hz, H-2), 5.93 (2 d, $J = 2.9$, $J' = 2.3$ Hz, H-1), and 8.77, 8.88, 8.92, and 9.00 (3 H, each, s, $\mathrm{CCH_3}$); *m/e* 190 (26, parent), 175 (69), 161 (100), 106 (55), 91 (31), and 78 (86); $\mathrm{uv_{max}}$ 278 nm (ϵ 2600). Thermolysis of **3**, either in glass, or on gas-chromatography columns, gave as sole product the isomer **5**: $\mathrm{ir}_{\max}^{\mathrm{film}}$ 1610, 1190, and 1050 cm^{-1}; nmr ($\mathrm{CCl_4}$) τ 3.98 and 4.01 (1 H, each, 2 d, $J = 9.8$ and 9.3 Hz, H-2 and H-6), 4.6–5.2 (2 H, 2 d of t, H-3 and H-5), 7.69 (2 H, t, $J = 7.0$ Hz, H-4, H-4′), and 8.70 and 8.92 (6 H each, s, $\mathrm{CCH_3}$); $\mathrm{uv_{max}}$ 281 nm (ϵ 3600); *m/e* 190 (84, parent), 175 (44), 174 (100), 159 (30), 106 (75), and 90 (48); $\mathrm{uv_{max}}$ 281 nm (ϵ 3600).

Irradiation of tropone with excess 1,1-dichloroethylene produced an unstable adduct which lost hydrogen chloride readily; neither the adduct nor its transformation product could be isolated pure. From irradiation of tropone with 1,1-diphenylethylene, tetrachloroethylene, cyclopentene, and diphenylacetylene, only unchanged **1** and tarry materials were obtained. However, irradiation of tropone in excess cyclopentadiene gave adduct **8**: bp 56–58° (0.4 mm) (41%); ir (film) 1638 (–OC=C), 1180 and 1078 (C—O) cm^{-1}; nmr ($\mathrm{CCl_4}$) τ 3.5–4.5 (4 H, m, H-3, 4, 5, 6), 4.4 (2 H, narrow m, cyclopentene vinyls), 4.8 (1 H, 2 d, $J = 9.5$, $J' = 2.6$ Hz, H-2), 5.8 (1 H, m, H-1), 6.4–7.1 (2 H, m, methines), and 7.2–7.4 (2 H, m, $-\mathrm{CH_2}$); *m/e* (parent) 172. The alternative 8 + 4 structure can be ruled out, since the signals for the cyclopentene vinyl and the bridge methylene hydrogens of such an adduct would be expected to appear at significantly lower and higher levels, respectively, than is observed for **8**.[7]

Mixtures of **1** with isobutene and tetramethylethylene underwent no reactions when stored in the dark. Irradiation of a tropone–isobutene mixture containing sufficient fluorenone to absorb ≥80% of the incident light resulted in formation of **2** at a rate only slightly less than that in the direct irradiation. These results favor the intermediacy of a tropone triplet excited state in the 8 + 2 additions observed here. It follows from the observed orientation in the adduct from isobutene that the first step in the process is bonding of the tropone oxygen atom to the terminal methylene group of the olefin. This argues that the reactive triplet in these additions is n → π* in nature, since 2 + 2 additions of saturated ketones and certain α,β-unsaturated ketones to olefins to give oxetanes, a process in which the reactive site is the carbonyl oxygen, is known to proceed *via* ketone n → π* triplets.[8] Experiments designed to more clearly delineate the scope of the addition and the nature of the reactive excited state are in progress.

Acknowledgment. I thank Otto Gansow for performing the double resonance experiments.

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(7) Dr. A. S. Kende has isolated an 8 + 2 adduct of tropone and furan, whose structure is evident from its nmr spectrum (private communication fom Dr. Kende).

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Probable Formation of 13-Atom Polyhedral Complexes Containing $\mathbf{B_{10}C_2H_{12}^{2-}}$ and Cobalt

Sir:

Previously, the largest known polyhedral carborane derivatives were icosahedral, 12-atom species typified by the $\mathrm{B_{10}C_2H_{12}}$ carboranes and transition metal derivatives of the $\mathrm{B_9C_2H_{11}^{2-}}$ dicarbollide ions.[1] We now wish to report the probable formation of 13-atom polyhedral complexes apparently generated with formal Co(III), π-bonded $\mathrm{C_5H_5^-}$, and the $\mathrm{B_{10}C_2H_{12}^{2-}}$ ion[2-4] formed by electron addition to 1,2-$\mathrm{B_{10}C_2H_{12}}$. The inclusion of the transition metal atom into the $\mathrm{B_{10}C_2H_{12}^{2-}}$ ion presumably completes a 13-atom polyhedron; Figure 1. The $\mathrm{B_{10}C_2H_{12}^{2-}}$ ion was produced by the reduction of 1,2-$\mathrm{B_{10}C_2H_{12}}$ at room temperature with 2 equiv of sodium in tetrahydrofuran with a

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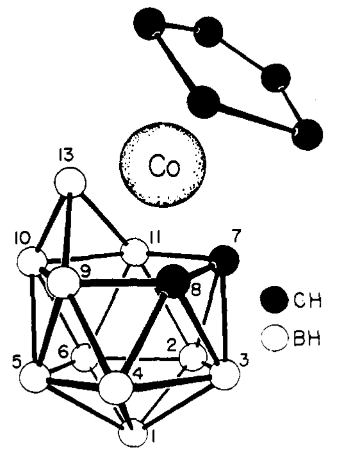

Figure 1. The proposed structure of π-cyclopentadienyl-π-dodecahydro-7,8-dicarba-*nido*-dodecaboratocobalt,$(C_5H_5)Co(7,8\text{-}B_{10}C_2H_{12})$.

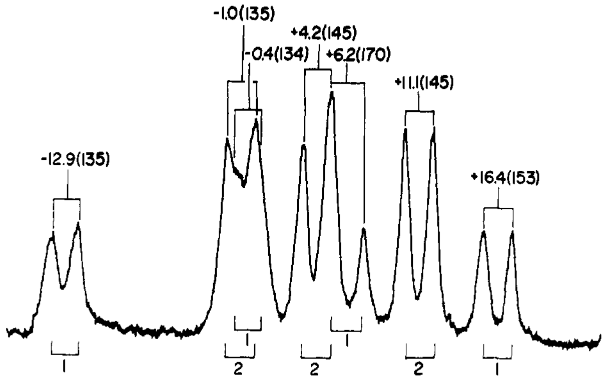

Figure 2. The 80.5-MHz ^{11}B nmr spectrum of $(C_5H_5)Co(7,8\text{-}B_{10}C_2H_{12})$ taken in acetone-d_6. Chemical shifts (parts per million relative to $BF_3 \cdot O(C_2H_5)_2$) and coupling constants (hertz) are indicated. Relative areas appear beneath the peaks.

catalytic amount of naphthalene. A threefold excess of NaC_5H_5 was added, followed by excess $CoCl_2$. The products were separated by column chromatography and recrystallized from hexane–dichloromethane solutions. The major products included π-cyclopentadienyl-π-undecahydro-7,8-dicarba-*nido*-undecaboratocobalt, $(C_5H_5)Co(7,8\text{-}B_9C_2H_{11})$ (1%),[1,5] a complex I formulated as π-cyclopentadienyl-π-dodecahydro-7,8-dicarba-*nido*-dodecaboratocobalt, $(C_5H_5)Co(7,8\text{-}B_{10}C_2H_{12})$ (50%), and a mixture of complex anions II which were isolated as their $(C_5H_5)_2Co^+$ and $(C_6H_5)_4As^+$ salts and formulated as $[(B_{10}C_2H_{12})_2Co^{III}]^-$ (12%). The red I was found to undergo a thermal rearrangement in hexane at reflux to an orange isomer III which subsequently undergoes further thermal rearrangement to a red-orange isomer IV in benzene at reflux. I, III, and IV have identical melting points of 250–251°, possibly due to the progressive thermal rearrangement in the solid phase of I → III → IV.

The 60-MHz ^1H nmr spectrum of I exhibited a sharp peak of area 5 at τ 4.48 and a broad peak of area 2 at τ 5.57 which were assigned to the cyclopentadienyl protons and the equivalent polyhedral C–H units, respectively. The 80.5-MHz ^{11}B nmr spectrum, Figure 2, consisted of doublets of area ratios 1:2:1:2:1:2:1, which is consistent with a molecule containing three unique pairs and four unique boron atoms.

The 60-MHz ^1H nmr of III consisted of a sharp peak of area 5 at τ 4.48 and two broad peaks of area 1 at τ 5.10 and 7.08, which were assigned to cyclopentadienyl protons and two types of polyhedral C–H units, respectively. The 80.5-MHz ^{11}B nmr spectrum contained doublets of area ratio 1:1:1:1:1:2:2:1 at −21.2 (140), −8.0 (138), −6.3 (149), −4.7 (140), +2.5 (170), +6.1 (170), +8.3 (161), and +12.8 (153) [chemical shift, parts per million relative to $BF_3 \cdot O(C_2H_5)_2$ (coupling constant, hertz)].

The 60-MHz ^1H nmr of IV consisted of a sharp peak of area 5 at τ 4.54 and two peaks of area 1 at τ 5.32 and 6.60 which were assigned to cyclopentadienyl protons and two types of polyhedral C–H units, respectively. The 80.5-MHz ^{11}B nmr consisted of ten doublets of equal area at −7.9 (145), −5.4 (169), −3.5 (145), −2.4 (161), +3.6 (145), +7.9 (145), +9.3 (169), +12.5 (145), +14.9 (145), and +16.9 (145).

The mass spectra of I, III, and IV were virtually identical and exhibited sharp cutoffs at *m/e* 270 which correspond to the $^{11}B_{10}{}^{12}C_7{}^1H_{17}{}^{59}Co^+$ ion. The electronic spectra and the chemical analyses are indicated in Tables I and II, respectively.

Table I. Electronic Spectra[a]

λ_{max}, mμ (ϵ)		
I	III	IV
450 (465)	446 (490)	475 (516)
296 (8850)	285 (8400)	279 (10,500)
256 (17,900)	254 (26,800)	252 (20,000)
230 (13,000) sh	225 (9100) sh	225 (11,000) sh

[a] Acetonitrile solution.

Table II. Chemical Analyses, %

		C	B	H	Co	As
I	Calcd	31.33	40.35	6.34	21.98	
	Found	31.61	40.12	6.88	21.76	
II	Calcd[a]	46.14	29.72	6.04	8.09	10.29
	Found	45.68	30.29	6.06	8.08	10.36
	Calcd[b]	31.33	40.35	6.34	21.98	
	Found	31.41	40.84	6.38	21.94	
III	Calcd	31.33	40.35	6.34	21.98	
	Found	31.52	39.77	6.55	21.86	
IV	Calcd	31.33	40.35	6.34	21.98	
	Found	31.36	40.20	6.50	21.85	

[a] Tetraphenylarsonium salt. [b] Cobalticinium salt.

The data presented indicate that III and IV are quite unsymmetrical but probably retain the gross structure of I and differ only in the position of the two carbon atoms in the polyhedral framework. A single-crystal X-ray diffraction study is in progress.

The direct reduction and transition metal complexation of $1,2\text{-}B_{10}C_2H_{12}$, as described here, and of $B_6C_2H_8$, as previously reported,[6,7] are being extended to include other carborane systems and transition metals other than cobalt.

Acknowledgment. The authors wish to thank Dr. R. J. Wiersema for measuring the ^{11}B nmr spectra and Professor F. A. L. Anet and Dr. C. Bradley for the use of

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(5) See *Inorg. Chem.*, 7, 1945 (1968), for nomenclature.

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the 80-MHz nmr spectrometer. This research was supported in part by the Office of Naval Research.

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Stoichiometry of the Chromic Acid Oxidation of Isopropyl Alcohol as a Function of Time. An Experimental Test of the Role of Chromium(IV)[1]

Sir:

The first step of the chromic acid oxidation by isopropyl and other secondary alcohols almost certainly leads to the formation of chromium(IV).[2] Watanabe and Westheimer[3] suggested several possible sequences for the subsequent reactions which account for two-thirds of the reaction product. Of these, the following two appeared the more reasonable

$$R_2CHOH + HCrO_4 + H^+ \rightleftharpoons R_2CHOCrO_3H + H_2O$$
$$R_2CHOCrO_3H \longrightarrow R_2C{=}O + Cr(IV)$$
$$Cr(IV) + Cr(VI) \longrightarrow 2Cr(V)$$
$$2(Cr(V) + R_2CHOH \longrightarrow Cr(III) + R_2C{=}O) \qquad (I)$$

$$R_2CHOH + HCrO_4^- + H^+ \rightleftharpoons R_2CHOCrO_3H + H_2O$$
$$R_2CHOCrO_3H \longrightarrow R_2C{=}O + Cr(IV)$$
$$R_2CHOH + Cr(IV) \longrightarrow R_2\dot{C}OH + Cr(III)$$
$$R_2\dot{C}OH + Cr(VI) \longrightarrow R_2C{=}O + Cr(V)$$
$$R_2CHOH + Cr(V) \longrightarrow R_2C{=}O + Cr(III) \qquad (II)$$

The reactions, particularly those involving cleavage of the reactant,[4] have frequently been considered in terms of mechanism I. However, Rocek and Radkowsky[5] as well as Nave and Trahanovsky[6] have presented evidence for Cr(IV) as an active oxidant and have favored mechanism II.

Our observation that chromium(V) may be observed spectrometrically during the oxidation of isopropyl alcohol in 97% acetic acid[7] permits a simple experimental differentiation between the two mechanisms. Qualitatively, one can see that in mechanism I the formation of 2 equiv of chromium(V) is accompanied by the formation of 1 equiv of acetone. Conversely, in mechanism II, the formation of 1 equiv of chromium(V) is accompanied by the formation of 2 equiv of acetone. Therefore, an investigation of the stoichiometry of the reaction at several points during its course would permit a differentiation between the two mechanisms.

This may also be stated in a more quantitative fashion. As indicated previously, we can calculate rate constants for the disappearance of both chromium(VI) and chromium(V) from spectrometric data. This may be done for each of the two models. Having the rate constants, the concentration of acetone may be calculated as a function of time giving the two curves in Figure 1. It can be seen that the per cent of acetone formed at any given time is quite different for the two mechanisms.

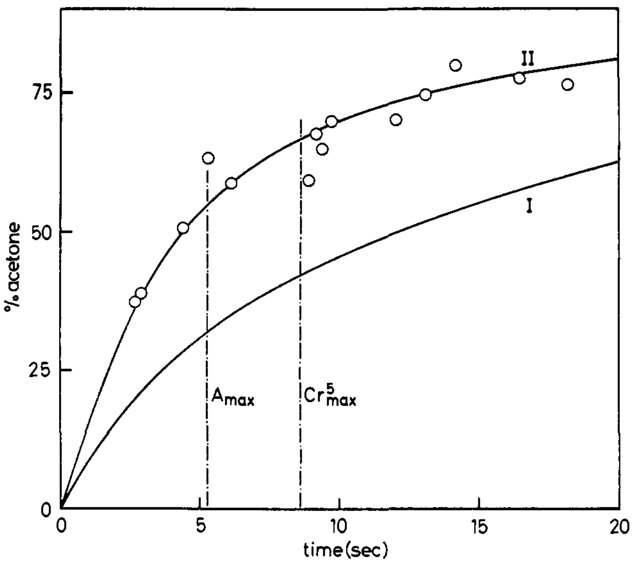

Figure 1. Rate of formation of acetone in the chromic acid oxidation of isopropyl alcohol in 97% acetic acid: [ROH] = 0.1258 *M*, [Cr(VI)] = 0.0050 *M*, [H$^+$] = 0.0125 *M*, μ = 0.184 (NaClO$_4$), T = 15 ± 0.05°, k_1 (disappearance of Cr(VI), appearance of Cr(V)) = 0.1455 sec^{-1}, k_2 (disappearance of Cr(V)) = 0.0355 sec^{-1}. Curve I is for Scheme I and curve II is for Scheme II.

The stoichiometry experiments were carried out in essentially the same fashion as the kinetic experiments,[7] except that the solutions were quenched with chromium(II) at different times.[8] The concentration of acetone in each solution was determined by gas chromatography using a 25% Carbowax 400 on C-22 Silocel and a flame ionization detector.[9] Methyl ethyl ketone was used as an internal standard. The per cent acetone formed, based on the amount found when the reaction was allowed to proceed to completion, is shown in Figure 1 as the open circles. The yield of acetone at complete reaction was found to be 1.50 ± 0.05 mol of acetone/mol of chromium trioxide used.

The experimental data give a good fit to the calculated curve for mechanism II. Figure 1 also contains lines indicating the time at which the absorbance at 510 mμ reaches a maximum and the time at which the concentration of chromium(V) reaches a maximum. At the absorbance maximum, 55% of the maximum amount of acetone had been formed, and at the chromium(V) maximum, 67% of the maximum amount of acetone had been formed.

The data clearly indicate that mechanism II is operative under the reaction conditions. The agreement with the previous results[5,6] suggests that mechanism II applies to all solutions containing at least a minimal amount of water. However, it does not apply to acetic acid–acetic anhydride mixtures in which chromium(IV) is found to be completely inactive as an oxidant.[10]

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