ion[2] and 1,3-$B_7C_2H_{13}$ are shown in Figure 1. It can be clearly seen that the 1,3-$B_7C_2H_{13}$ structural framework is obtained if the two boron atoms removed during the oxidation are boron atoms 4 and 8.

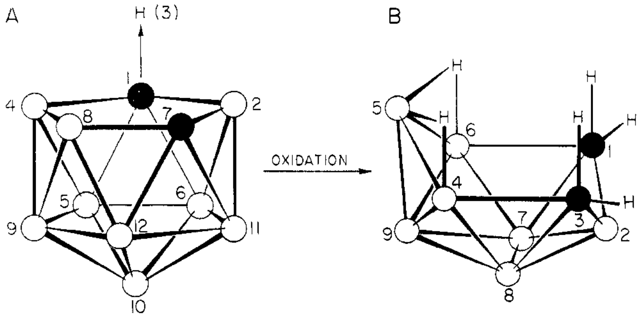

Figure 1.—(A) Structure of the (3)-1,7-$B_9C_2H_{12}^-$ ion. (B) Structure of 1,3-$B_7C_2H_{13}$: ○, BH; ●, carbon.

Recently, Papetti, *et al.*,[3] developed a hot flow-tube method for accomplishing the rearrangement of 1,2-$B_{10}C_2H_{12}$ to 1,7-$B_{10}C_2H_{12}$. The ethanolic potassium hydroxide degradation[2] of 1,7-$B_{10}C_2H_{12}$ to yield (3)-1,7-$B_9C_2H_{12}^-$ was reexamined, and it was found that the (3)-1,7-$B_9C_2H_{12}^-$ ion could be prepared in 89% yield by heating an ethanolic potassium hydroxide solution of 1,7-$B_{10}C_2H_{12}$ for 40 hr at the reflux temperature. The oxidation of the (3)-1,7-$B_9C_2H_{12}^-$ ion is now the preferred method of preparing 1,3-$B_7C_2H_{13}$ in this laboratory.

Experimental Section

1,7-Dicarba-*closo*-dodecaborane(12) was prepared by the method of Papetti, *et al.*[3] Methylene chloride was solvent grade and all other reagents were reagent grade and were used without further purification.

All reactions were conducted under a nitrogen atmosphere and subsequent product work-up of the 1,3-$B_7C_2H_{13}$ required a nitrogen atmosphere.

Preparation of Potassium (3)-1,7-Dicarba-*nido*-dodecahydroundecaborate(−1).—Into a 1-l. flask flushed with nitrogen was placed 50 g (0.89 mol) of potassium hydroxide dissolved in 500 ml of absolute ethanol. To this solution was added 50.0 g (0.345 mol) of 1,7-$B_{10}C_2H_{12}$ and the resulting solution was heated under nitrogen for 40 hr at the reflux temperature. After cooling, sufficient water (*ca.* 600 ml) was added to precipitate the unreacted carborane which was extracted from the aqueous ethanolic solution with four 150-ml portions of *n*-hexane. The *n*-hexane solution was dried over anhydrous magnesium sulfate, filtered, and evaporated to dryness yielding 12.0 g (0.083 mol) of 1,7-$B_{10}C_2H_{12}$. The aqueous ethanolic phase was evaporated to dryness and the residual solid was dissolved in 150 ml of methanol. To this methanol solution was added 90 g of powdered Dry Ice followed by 500 ml of ether with stirring. The precipitated K_2CO_3 was separated by filtration and thoroughly washed with ether; the solution was evaporated to an oil, to which an additional 500 ml of ether was added, and the remaining K_2CO_3 was separated by filtration. The ether solution was evaporated to a low volume and the product was transferred to a Dean–Stark distillation apparatus. The residual ether, alcohol, and water were distilled using toluene as the carrier. The white crystalline product was separated by filtration and dried under high vacuum for several hours yielding 40.0 g (0.232 mol) or 89% of the potassium salt based on the quantity of 1,7-$B_{10}C_2H_{12}$ consumed. The product was identified by its infrared and ^{11}B nmr spectra.

Preparation of 1,3-Dicarba-*nido*-nonaborane(13).—Into a 2-l. three-necked, round-bottom flask equipped with a mechanical stirrer, addition funnel, and N_2 inlet was placed 20.0 g (0.116 mol) of (3)-1,7-$KB_9C_2H_{12}$ dissolved in 100 ml of water. To this solution was added 200 ml of methylene chloride and 200 ml of 2 *N* H_2SO_4. The resulting mixture was flushed with nitrogen and maintained at 0°. A dichromate solution consisting of 35 g (0.118 mol) of $Na_2Cr_2O_7 \cdot 2H_2O$ in 500 ml of 2 *N* H_2SO_4 was added dropwise with rapid stirring. The addition time was 2 hr. At once after complete addition, the two phases were separated and the aqueous phase was washed four times with 75-ml portions of methylene chloride. The combined methylene chloride extracts were washed once with water, dried over anhydrous magnesium sulfate, filtered, and evaporated on a mechanical pump to a low volume. The remaining solvent was removed under high vacuum on a sublimation apparatus, and the product was sublimed at 50° to a −80° cold finger. The yield was 10.1 g or 76%, and the product was identified by its infrared and ^{11}B nmr spectra.

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Decarbonylation of Molybdenum Acetyl Complexes

BY KENNETH W. BARNETT

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The reaction of π-$C_5H_5Mo(CO)_3CH_3$ with triphenylphosphine in refluxing tetrahydrofuran or hexane affords mixtures of π-$C_5H_5Mo(CO)_2(P(C_6H_5)_3]COCH_3$ and π-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]CH_3$. The σ-methyl complex appears to arise *via* decarbonylation of the acetyl derivative.[1] Similar investigations in other laboratories,[2–5] carried out with a variety of phosphorus ligands, led to other acetyl complexes of the formula π-$C_5H_5Mo(CO)_2(L)COCH_3$, but the decarbonylation reactions were not observed in these studies. This is apparently due to the relatively mild conditions and/or short reaction times employed; in one instance[5] the decarbonylation was purposely avoided.

We have now investigated the course of the reactions of π-$C_5H_5Mo(CO)_3CH_3$ with the donor ligands $P(C_6H_5)_3$, $P(OC_6H_5)_3$, $P(n\text{-}C_4H_9)_3$, and $P(OCH_3)_3$ *via* proton nmr spectroscopy. We find that the decarbonylation reactions

$$\pi\text{-}C_5H_5Mo(CO)_2(L)COCH_3 \longrightarrow \pi\text{-}C_5H_5Mo(CO)_2(L)CH_3 + CO$$

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TABLE I

PROTON NMR DATA FOR π-$C_5H_5Mo(CO)_2(L)R$ COMPLEXES[a]

L	R	τ[b]		
		C_5H_5	L	CH_3
$P(C_6H_5)_3$	$COCH_3$	5.21 (J_{PH} = 1.0)	2.7 (M)	7.19 (S)
$P(C_6H_5)_3$	CH_3	5.55 (J_{PH} = 1.5)	2.7 (M)	9.61 (D, J_{PH} = 3.0)
$P(OC_6H_5)_3$	$COCH_3$	5.14 (J_{PH} = 1.0)	2.7 (M)	7.80 (S)
$P(OC_6H_5)_3$	CH_3	5.40 (J_{PH} = 1.5)	2.7 (M)	9.73 (D, J_{PH} = 3.0)
$P(OCH_3)_3$	$COCH_3$	4.72 (J_{PH} = 1.5)	6.38 (D, $J_{PH} \cong 10$)	7.53 (S)
$P(OCH_3)_3$	CH_3	4.88 (J_{PH} = 1.5)	6.45 (D, $J_{PH} \cong 10$)	9.78 (D, J_{PH} = 3.0)
$P(n\text{-}C_4H_9)_3$	$COCH_3$	4.88 (J_{PH} = 1.0)	8.5, 9.1 (M)	7.53 (S)
$P(n\text{-}C_4H_9)_3$	CH_3	5.03 (J_{PH} = 1.5)	8.5, 9.1 (M)	9.87 (D, J_{PH} = 2.5)

[a] Deuterioacetonitrile solvent, Varian Associates A-60 spectrometer, and τ 10 for tetramethylsilane. [b] All C_5H_5 resonances appear as doublets. Otherwise, S = singlet, D = doublet, M = multiplet; coupling constants are in cycles per second.

occur in each case, even when carbon monoxide is prevented from escaping the system.

Typically the reactants (1:1 molar ratio) and acetonitrile-d_3 are charged under nitrogen to an nmr tube which is sealed immediately and warmed to 60°. Initial ligand and molybdenum complex concentrations are on the order of 0.25 *M*. Regardless of the ligand employed, the characteristic[1,5] resonances of the π-$C_5H_5Mo(CO)_2(L)COCH_3$ complexes appear within 30 min (Table I).

Resonances corresponding to the π-$C_5H_5Mo(CO)_2(L)CH_3$ species first appear after 6.5, 7.0, 12.0, and 4.0 hr for the systems where L = $P(C_6H_5)_3$, $P(OC_6H_5)_3$, $P(OCH_3)_3$, and $P(n\text{-}C_4H_9)_3$, respectively. In all cases the decarbonylations proceed smoothly with the ratio $[\pi\text{-}C_5H_5Mo(CO)_2(L)COCH_3]/[\pi\text{-}C_5H_5Mo(CO)_2(L)CH_3]$ decreasing with increasing time (Table II). Only when L = $P(C_6H_5)_3$ are significant quantities of π-$C_5H_5Mo(CO)_3CH_3$ observed after 30 hr of contact time. The failure of this reaction to go to completion in a closed system was noted in an earlier kinetic study.[4]

The data of Table II demonstrate that the decarbonylation reactions are much slower than are the initial ligand substitutions. The final data (Table II) for L = $P(C_6H_5)_3$ and $P(n\text{-}C_4H_9)_3$ represent approximate steady-state concentrations as the relative proportions of products in these cases do not change significantly (±3%) at 75–100 hr. Values at reaction times longer than 30 hr for the triphenyl and trimethyl phosphite systems are unreliable owing to apparent thermal decomposition of the complexes. This is not the case for the other ligand systems, in which the resonances remain sharp indefinitely and no spurious peaks appear in the spectra.

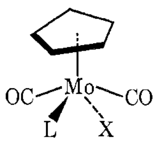
TABLE II

DISTRIBUTION OF π-$C_5H_5Mo(CO)_3CH_3$, π-$C_5H_5Mo(CO)_2(L)COCH_3$, AND π-$C_6H_5Mo(CO)_2(L)CH_3$ COMPLEXES AS A FUNCTION OF TIME[a,b]

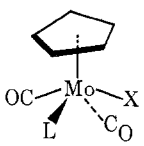
Ligand	Time, hr	π-$C_5H_5Mo(CO)_3CH_3$	π-$C_5H_5Mo(CO)_2(L)COCH_3$	π-$C_5H_5Mo(CO)_2(L)CH$
$P(C_6H_5)_3$	0.5	75	25	0
	2.0	39	61	0
	6.5	32	50	18
	30.0	25	43	32
$P(OC_6H_5)_3$	0.75	~40	~60	0
	1.0	~15	~85	0
	1.25	<5	>95	0
	2.5	0[c]	100	0
	4.5	0	100	0
	7.0	0	>95	<5
	30.0	0	85	15
$P(OCH_3)_3$	0.67	~40	~60	0
	1.0	~10	~90	0
	1.25	0[c]	100	0
	6.0	0	100	0
	12.0	0	>95	<5
	22.0	0	84	16
	47.0	0	57	43
$P(n\text{-}C_4H_9)_3$	0.75	~50	~50	0
	1.0	~25	~75	0
	1.5	0[c]	100	0
	3.0	0	100	0
	4.0	0	>95	<5
	23.0	0	87	13
	47.0	0	76	24

[a] Based on relative areas of π-C_5H_5 resonances; the CH_3 resonance areas are in qualitative agreement. [b] Deuterioacetonitrile solvent; original π-$C_5H_5Mo(CO)_3CH_3$ and ligand concentrations are 0.25 *M*. [c] Although listed as absent, 2–3% π-$C_5H_5Mo(CO)_3CH_3$ was observed in some of the spectra.

The stereochemical course of these decarbonylations also deserves comment. In complexes of the general formula π-$C_5H_5Mo(CO)_2(L)X$ the carbonyl groups may occupy relative *cis* or *trans* positions



trans



cis

Either isomer should afford two infrared-active CO stretching modes. Manning[6] has shown from geometric considerations that *trans* stereochemistry should result in the lower frequency band being the more intense and *vice versa* for *cis* complexes. In addition, *trans* derivatives (L = a phosphine or phosphite) afford doublet cyclopentadienyl resonances in their proton nmr spectra, while the corresponding resonances are unsplit in *cis* complexes.[6,7] In cases where both isomers of a given complex are produced, the chemical shifts of π-C_5H_5 protons of *cis* and *trans* isomers differ by 0.1–0.3 ppm. The reasons for these differences in multiplicity and chemical shift remain obscure.

On the basis of both ir and nmr criteria, all of the acetyl derivatives π-$C_5H_5Mo(CO)_2(L)COCH_3$ have been assigned *trans* structures in solution.[5] These data

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(6) A. R. Manning, *J. Chem. Soc., A*, 651 (1968), and references therein.

(7) A. Bainbridge, P. J. Craig, and M. Green, *ibid., A*, 2715 (1968).

were collected at 30° and our current findings at 60° are in accord with these assignments. An X-ray diffraction study revealed that π-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]COCH_3$ possesses *trans* stereochemistry in the solid state.[8] The methyl derivatives described here afford doublet C_5H_5 resonances (Table I) and two terminal CO bands (1935–1950 and 1845–1855 cm^{-1}) of which the lower frequency absorption is the more intense. Thus the over-all transformations may be described by

$$trans\text{-}\pi\text{-}C_5H_5Mo(CO)_2(L)COCH_3 \xrightarrow{-CO} trans\text{-}\pi\text{-}C_5H_5Mo(CO)_2(L)CH_3$$

The detailed mechanism of these reactions must await further investigation, but certain features should be mentioned at present. The carbonyl group lost on decarbonylation is probably not the acetyl CO, but rather a terminal ligand, as found in acylmanganese[9] and -cobalt[10] carbonyl systems. Furthermore, we have found that a mixture of *cis*- and *trans*-π-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_3$ (synthesized from π-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]^-Na^+$ and CH_3I[11]) maintains a constant *cis*:*trans* ratio under our reaction conditions for up to 48 hr as shown by nmr. Thus the *cis*-methyl complex should have been observed if formed during decarbonylation. We have as yet been unable to rigorously exclude the possibility of *cis–trans* equilibration of the corresponding acetyl derivative π-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]COCH_3$ prior to decarbonylation owing to the unexpectedly complex reaction of the anion π-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]^-$ with acetyl chloride.

Craig and Green have recently reported the solid-state (140°) decarbonylation of *trans*-π-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]COCH_2C_6H_5$ to the corresponding σ-benzyl complex, the latter of indeterminate stereochemistry.[12] The relationship of this finding to our results is not clear at present.

Experimental Section

Materials.—The complex π-$C_5H_5Mo(CO)_3CH_3$ was prepared by the published method.[13] Triphenylphosphine was used as received from Eastman Chemicals. Triphenyl phosphite, trimethyl phosphite, and tributylphosphine were obtained from Eastman, Bryant, and M and T, respectively, and distilled under nitrogen prior to use. Acetonitrile-d_3 was purchased from Diaprep, inc., and used without further purification.

General Procedure.—In the drybox (Vacuum Atmospheres Corp), 0.2 g of π-$C_5H_5Mo(CO)_3CH_3$ (0.77 mmol) and an equimolar amount of the ligand were dissolved in acetonitrile-d_3 (3.0 ml) and equal portions were charged to each of two nmr tubes. Tetramethylsilane was added as an internal marker and the tubes were capped immediately. The sample tubes were quickly brought out of the drybox and frozen immediately in liquid nitrogen. The tubes were then inserted into a standard vacuum line apparatus and sealed (while still frozen). The samples were allowed to warm slowly to room temperature and an initial nmr spectrum was obtained (Varian Associates A-60 spectrometer). Thereafter, the sample tubes were thermostated at 60 ± 2° for the duration of the experiment. The spectra of the π-$C_5H_5Mo(CO)_3CH_3$–$(C_6H_5)_3P$ reaction mixtures were obtained at 60° for reasons of solubility, but all other nmr spectra were obtained at ambient temperatures. Samples of the π-$C_5H_5Mo(CO)_2(L)CH_3$ compounds for infrared analysis (Beckman IR-4, cyclohexane solution) were obtained by refluxing the corresponding acetyl complex in acetonitrile (open system) for 50–60 hr. The identities of the products were further verified by recording their nmr spectra.

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Metal–Metal Frequencies and Force Constants of $Ir_4(CO)_{12}$[1]

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As part of a continuing study of frequencies and force constants associated with the vibrational modes of metal atom clusters[2,3] we present here an analysis of the low-frequency Raman spectrum of $Ir_4(CO)_{12}$. This molecule contains a tetrahedral cluster of iridium atoms, with all carbonyl ligands bound terminally,[4] as shown in Figure 1. In a preliminary report,[3] three intense Raman bands, at 208, 164, and 105 cm^{-1}, were identified with the anticipated cluster modes, of symmetries A_1, T_2, and E, respectively. The frequency ratios are not far from those predicted from a "simple cluster" model:[3] $\nu_{A_1}:\nu_{T_2}:\nu_E = 2:\sqrt{2}:1$.

These frequencies have been corroborated by Abel, *et al.*,[5] who found the 164-cm^{-1} band in the infrared as well, confirming its assignment to a T_2 mode. Abel, *et al.*, also reported higher frequency fundamentals for $Ir_4(CO)_{12}$ and discussed them briefly. Our spectra (Raman and infrared) are in good agreement with theirs.

The representations of the T_d point group spanned by a complete set of internal coordinates are given in Table I. Below 250 cm^{-1} nine Raman bands are expected, from vibrations primarily involving metal–metal stretching (three) and metal–carbon deformation (six).

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