respectively. Because the experimental values of $\phi_{TS}(T)$ are in good accord with those calculated, we consider that $k_N = 0$ holds in the temperature range studied, as assumed above. It, therefore, is likely that the photoexcited ClCr^{III}(TPP)Ac is fated to undergo the dissociation of the axial acetone or result in the formation of the $^4T_1$ state.

When the $^4T_1$ state is formed, the $^6T_1$ state is populated, leading to establishment of Boltzmann equilibrium between the $^4T_1$ and $^6T_1$ states.[3] As will be mentioned later, the excited state detected by laser photolysis of ClCr^{III}(TPP)Ac is principally ascribed to the $^6T_1$ state. At room temperature, the lifetime of the $^6T_1$ state is too short, less than 100 ns, to determine precisely the decay rate constant by our laser system. However, laser photolysis at lower temperatures enables us to observe the decay profile of the transient spectrum of the $^6T_1$ state. In the temperature range 180-230 K, we could measure the decay rate constants of the $^6T_1$ state, k_{obsd}, represented as[3]

$$k_{\text{obsd}} = (k_S + \chi k_Q)(1 + \chi)^{-1} \qquad (16)$$

where

$$\chi = \tfrac{2}{3} \exp(-\Delta E_{QS}/RT) \qquad (17)$$

On the assumption $\chi \ll 1$, eq 16 will be transformed to

$$\ln (k_{\text{obsd}} - k_S) = \ln (\tfrac{2}{3}k_Q) - \Delta E_{QS}R^{-1}T^{-1} \qquad (18)$$

With the use of $k_S = 4.4 \times 10^5\ \text{s}^{-1}$, the plot of $\ln (k_{\text{obsd}} - k_S)$ vs T^{-1} gave a straight line. From the slope and intercept of the line, we obtained the following values:

$$\Delta E_{QS} = 770\ \text{cm}^{-1} \qquad k_Q = 8.9 \times 10^8\ \text{s}^{-1}$$
$$k_S = 4.4 \times 10^5\ \text{s}^{-1}$$

Because the values of χ can be calculated with the obtained value of ΔE_{QS} (770 cm^{-1}) as $\chi = 10^{-3}$–$10^{-4} \ll 1$ in the temperature range 180-295 K, the assumption $\chi \ll 1$ used in derivation of eq 18 is appropriate. The value of χ stands for the ratio of the population of the $^4T_1$ state to that of the $^6T_1$ state. Thus, the observed excited state detected after laser irradiation of ClCr^{III}(TPP)Ac is concluded to be the $^6T_1$ state.

Gouterman et al.[3] reported the value of ΔE_{QS} as 520 cm^{-1} by measuring dual luminescence around 815 and 850 nm from the $^4T_1$ and $^6T_1$ states of ClCr^{III}(TPP), respectively, in a mixture of 1-butanol and 3-methylpentane in the wide temperature range 300-1.8 K. It was difficult for us to detect luminescence in an acetone solution of ClCr^{III}(TPP)Ac at room temperature. However, at 180 K, weak luminescence with a peak around 825 nm was clearly observed, which is probably from the $^4T_1$ state. From the luminescence peak of the $^4T_1$ state and the value of ΔE_{QS} = 770 cm^{-1}, luminescence from the $^6T_1$ state in acetone is expected to be observed at 880 nm. However, no luminescence from the $^6T_1$ state could be detected at temperatures higher than the freezing point of acetone (178 K). Below 180 K, we were unable to observe luminescence from an acetone solution because acetone is opaque below its freezing point.

Conclusion

The acetonate of ClCr^{III}(TPP), ClCr^{III}(TPP)Ac, photodissociates the axial ligand, Ac, via the $^4S_1$ state with a quantum yield of ca. 0.6 at 295 K independent of irradiation wavelength, 355 or 532 nm. The activation energy for the dissociation of Ac in the $^4S_1$ state is obtained as 2.6 kcal/mol.

From the quantum yield measurements for photodissociation of Ac and the formation of the $^4T_1$ state in the temperature range 180-295 K, it is revealed that no radiationless transition occurs from the $^4S_1$ state to the ground state.

The energy gap between the $^4T_1$ and $^6T_1$ states in acetone is evaluated as 770 cm^{-1} on the basis of measurements of the decay rate constants of the $^6T_1$ state in the temperature range 180-230 K.

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Contribution from the Department of Chemistry,
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Reduction of BH$_3$·THF by Alkali Metal (K, Rb, Cs) and Ytterbium Mercury Amalgams To Form Salts of [B$_3$H$_8$]$^-$: A Simple Procedure for the Synthesis of Tetraborane(10)

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The octahydrotriborate(1−) ion, [B$_3$H$_8$]$^-$, is employed in a wide variety of applications: syntheses of novel metallaborane,[1] higher borane,[2] heteroatom borane,[3] and carborane cluster compounds;[4] the reduction of a wide variety of organic compounds;[5] the preparation of electrode coatings through reduction reactions;[6] applications to explosive and propellant technology;[7] neutron capture therapy;[8] and serum triglyceride and serum cholesterol biological studies.[9]

A number of procedures have been reported for the preparation of [B$_3$H$_8$]$^-$ salts.[10-15] Of these, the most common starting points involve the reaction of sodium borohydride with boron trifluoride etherate[16] or the reaction of sodium borohydride with iodine.[7] However, Na[B$_3$H$_8$] is highly solvated by the ether solvent in these reactions, making it difficult to measure, accurately, amounts of

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this salt if it is to be used for further chemical reactions. It is generally converted to tetraalkylammonium,[12,19,20] amino, phosphino,[18] other alkali-metal,[16,20] or thallium[20] salts by metathesis reactions.

Alkali-Metal Salts of $[B_3H_8]^-$. The salts $M[B_3H_8]$ (M = K, Rb, Cs) were prepared by the reduction of BH_3THF by potassium, rubidium, and cesium amalgams (eq 1). These alkali-metal

$$2\mathrm{M/Hg} + 4\mathrm{BH_3THF} \xrightarrow{\mathrm{THF}} \mathrm{M[BH_4]} + \mathrm{M[B_3H_8]} \tag{1}$$

$[B_3H_8]^-$ salts are soluble in THF while the $[BH_4]^-$ salts are not, thereby allowing an easy separation of products. The procedure resembles that for the preparation of $Na[B_3H_8]$[10] by the reduction of B_2H_6 by sodium amalgam in diethyl ether, but has the advantages of being a more rapid reaction, providing a virtually solvent-free product, and providing simpler routes to these salts than previously described.[16,20] Furthermore, for most, if not all applications, $Tl[B_3H_8]$ can be replaced by the alkali-metal octahydrotriborates described here. Thallium octahydrotriborate is a useful starting material in the preparation of derivatives of $[B_3H_8]^-$ through metathesis reactions,[20] but because of the toxicity of thallium,[21] this salt is particularly hazardous.

Two possible routes for the formation of $[B_3H_8]^-$ can be considered. One route is that proposed by Hermanek and Plesek.[25] It involves the initial formation of $[BH_3]^-$ radical anions that combine to form $[B_2H_6]^{2-}$, which is then involved in the sequence represented by eq 2 and 3. Another possible route involves the

$$[\mathrm{B_2H_6}]^{2-} + \mathrm{THF{\cdot}BH_3} \xrightarrow{\mathrm{THF}} [\mathrm{B_3H_9}]^{2-} + \mathrm{THF} \tag{2}$$

$$[\mathrm{B_3H_9}]^{2-} + \mathrm{THF{\cdot}BH_3} \xrightarrow{\mathrm{THF}} [\mathrm{B_3H_8}]^{-} + [\mathrm{BH_4}]^{-} \tag{3}$$

formation of the dianion $[BH_3]^{2-}$, which then reacts with $THF{\cdot}BH_3$ to produce the intermediate $[B_2H_6]^{2-}$.

Boron-11 and proton NMR spectra of the isolated octahydrotriborate(1−) salts are nonets and decets, respectively, consistent with NMR spectra of $Na[B_3H_8]$,[22,26] and show little or no impurities even before they are recrystallized. Infrared spectra of the salts recrystallized from THF/Et_2O at room temperature give no evidence for retention of solvent. Analyses indicate carbon contents of less than 1%.

$(THF)_xYb[B_3H_8]_2$. The lanthanide metal ytterbium is a strong reducing agent as an amalgam, effectively equivalent to the s-block metals in its reactivity.[22] This amalgam reduces $BH_3{\cdot}THF$ in a manner analogous to that cited in reaction 1. Ytterbium octahydrotriborate was formed according to eq 4. Unlike the alka-

$$2\mathrm{Yb/Hg} + 8\mathrm{BH_3{\cdot}THF} \xrightarrow{\mathrm{THF}} \mathrm{Yb[BH_4]_2} + \mathrm{Yb[B_3H_8]_2} + \mathrm{THF} \tag{4}$$

li-metal salts, $(THF)_xYb[BH_4]_2$ is more soluble in THF than $(THF)_xYb[B_3H_8]$. Separation of $(THF)_xYb[B_3H_8]$ from $(THF)_xYb[BH_4]_2$ by fractional crystallization was confirmed by its ^{11}B NMR spectrum, which consists of a nonet. In THF, this salt exhibits a light green color. When THF is exchanged with CH_3CN the solution turns orange. Yield data were not obtained because complete removal of the solvent leads to decomposition of the salts. Both $(THF)_xYb[B_3H_8]_2$ and $(THF)_xYb[BH_4]_2$ are extremely air and moisture sensitive.

B_4H_{10}. A previously reported method for the preparation of B_4H_{10} involves the reaction of $[NEt_4][B_3H_8]$ with BCl_3 and also BF_3 in the absence of a solvent (eq 5).[18b] This synthesis is not

$$2[\mathrm{B_3H_8}]^- + 2\mathrm{BX_3} \rightarrow \mathrm{B_4H_{10}} + (1/n)(\mathrm{B_2H_4})_n + [\mathrm{HBX_3}]^- \tag{5}$$

$$\mathrm{X = Cl, F}$$

effective when $Na[B_3H_8]$ is employed because retained ethereal solvent interferes with the desired reaction of $[B_3H_8]^-$ with boron halide. Availability of effectively solvent-free $K[B_3H_8]$ obtained from reaction 1 facilitates the synthesis of B_4H_{10} through reactions with gaseous BF_3 and also BCl_3. Yields of 55% and 51%, respectively, of the boron in $[B_3H_8]^-$ are equivalent to those obtained from tetraalkylammonium salts of $[B_3H_8]^-$.[2e,18b] The theoretical yield of B_4H_{10} based upon eq 5 is 67% of the boron in $[B_3H_8]^-$. Ease of preparation of $K[B_3H_8]$ as described here and the fact that the synthesis of B_4H_{10} does not require a solvent attest to the utility of this method.

Experimental Section

All manipulations were carried out on a standard high-vacuum line or in a drybox under an atmosphere of pure, dry N_2. Tetrahydrofuran (THF) and Et_2O were dried by distillation from sodium benzophenone ketyl and stored in bulbs containing sodium benzophenone ketyl that were equipped with Teflon stopcocks. CH_3CN was dried for 2–3 days over P_4O_{10} with constant stirring and then transferred, by distillation, to a storage bulb. $BH_3{\cdot}THF$ (Aldrich Chemical) was obtained as a 1.0 M solution and used as received. K (Aldrich) was received as sticks or chips in mineral oil and was washed with hexanes before use. Na (Aldrich), Rb, Cs, and Yb (Strem) were used as received and stored in the drybox. Triply distilled mercury was used as received from Bethlehem Instruments. BCl_3 and BF_3 (Matheson Gas Products) were passed through a U-trap maintained at −78 °C and stored at −196 °C in a Pyrex tube fitted with a Teflon stopcock.

Boron-11 NMR ($\delta(BF_3OEt_2)$ = 0.00 ppm) and ^1H NMR (δ(TMS) = 0.00 ppm) spectra were obtained on a Bruker 250 NMR spectrometer at 80.25 and 250 MHz, respectively. IR spectra were obtained on a Fourier transform Mattson IR Polaris spectrometer. Elemental analyses were performed by Analytische Laboratorien, Gummersbach, Germany.

Preparation of $M[B_3H_8]$ (M = K, Rb, Cs). Typically, in the drybox, 3 mmol of metal (K, 0.117 g; Rb, 0.256 g; Cs, 0.399 g) was added to 3–5 mL of triply distilled Hg in a Pyrex flask containing a glass-coated stir bar and fitted with a Teflon stopcock. The amalgam was allowed to stir for 2 h in vacuo. As the amalgam formed, the Hg wetted the glass. The flask was returned to the drybox where 9.0 mL of $BH_3{\cdot}THF$ solution was added by syringe. The flask was then cooled to −196 °C, degassed and allowed to warm to room temperature. The reaction mixture was stirred for ca. 17 h, during which time the solution turned from dark gray to a silky white suspension. The solution was transferred by pipet to a vacuum extractor. Borohydride salt was removed by filtration of the solution. This precipitate was then washed with 10 mL of THF to remove any remaining $[B_3H_8]^-$. Borohydride salts were identified by their ^{11}B NMR[23] and IR spectra.[24] The THF was then removed under dynamic vacuum overnight; a white solid remained behind. The $M[B_3H_8]$ was then recrystallized from THF/Et_2O.

$K[B_3H_8]$. Yield: 45% (0.107 g, 1.35 mmol). ^{11}B NMR spectrum in THF-d_8: −30.5 ppm (nonet, J = 33 Hz). ^1H NMR spectrum in THF-d_8: 0.2 ppm (decet, J = 33 Hz). IR spectrum (Nujol, NaCl plates): 2475 (s), 2432 (vs), 2376 (s), 2338 (s), 2226 (vw), 2212 (vw), 2134 (w), 2100 (w), 1176 (s), 1009 (s) 738 (w) cm^{-1}. X-ray (Cu Kα) powder pattern, d, Å (I): 5.47 (M), 4.55 (W), 4.09 (VS), 3.69 (S), 3.62 (S), 2.74 (MS), 2.60 (M), 2.53 (M), 2.45 (MS), 2.27 (M), 2.16 (W), 1.93 (W). Anal. Calcd for $K[B_3H_8]$: K, 49.12; B, 40.75. Found: K, 48.80; B, 40.47; C, 0.24.

$Rb[B_3H_8]$. Yield: 53% (0.200 g, 1.59 mmol). ^{11}B NMR spectrum in THF-d_8: −30.3 ppm (nonet, J = 33 Hz). ^1H NMR spectrum in THF-d_8: 0.2 ppm (decet, J = 33 Hz). IR spectrum (Nujol, NaCl plates): 2476 (vs), 2427 (vs) 2367 (vs), 2335 (vs), 2240 (vw), 2232 (vw), 2128 (w), 2092 (w), 1176 (s), 1008 (s), 787 (w) cm^{-1}. X-ray (Cu Kα) powder pattern, d, Å (I): 5.43 (M), 4.62 (VS), 4.25 (S), 4.17 (M), 3.75 (S), 3.63 (S), 3.36 (W), 2.98 (W), 2.76 (MS), 2.60 (S), 2.52 (MS), 2.34 (W), 2.30 (W), 2.25 (W), 2.21 (M), 1.98 (VW), 1.83 (VW), 1.80 (VW), 1.77 (VW), 1.68 (W), 1.64 (VW), 1.62 (VW). Anal. Calcd for $Rb[B_3H_8]$: Rb, 67.89; B, 25.73. Found: Rb, 67.30; B, 25.18; C, 0.77.

$Cs[B_3H_8]$. Yield: 40% (0.208 g, 1.2 mmol). ^{11}B NMR spectrum in THF-d_8: −29.8 ppm (nonet, J = 33 Hz). ^1H NMR spectrum in THF-d_8: 0.1 ppm (decet, J = 33 Hz). IR spectrum (Nujol, NaCl plates): 2470 (s), 2416 (vs), 2361 (s), 2327 (s), 2238 (vw), 2123 (w), 2082 (w), 1170 (s), 1006 (s), 736 (w) cm^{-1}. X-ray (Cu Kα) powder pattern, d, Å (I):

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5.57 (W), 4.69 (VS), 4.39 (M), 4.31 (W), 3.83 (M), 3.69 (M), 3.44 (VW), 3.08 (VW), 2.82 (W), 2.67 (S), 2.60 (S), 2.43 (W), 2.37 (W), 2.29 (S), 2.10 (W), 2.04 (W).

K[BH$_4$]. ^{11}B NMR spectrum in D_2O: −43.0 ppm (quintet, J = 80 Hz). IR spectrum (KBr pellet): 1120 (vs), 2215 (s), 2289 (vs), 2379 (s) cm^{-1}.

Rb[BH$_4$]. ^{11}B NMR spectrum in D_2O: −42.5 ppm (quintet, J = 80 Hz). IR spectrum (KBr pellet): 1112 (vs), 2203 (vs), 2277 (vs), 2356 (s), 2356 (s) cm^{-1}.

Cs[BH$_4$]. ^{11}B NMR spectrum in D_2O: −42.0 ppm (quintet, J = 81 Hz). IR spectrum (KBr pellet): 1099 (vs), 2180 (s), 2249 (vs), 2289 (vs), 2334 (s) cm^{-1}.

Preparation of Yb[B$_3$H$_8$]$_2$. An amalgam of ytterbium metal was formed in the same manner as the alkali-metal amalgams with the exception that 15 h of stirring was required for complete formation. A 6:1 molar ratio of BH_3·THF to metal was used to form (THF)$_x$Yb[B$_3$H$_8$]$_2$ complexes. By fractional crystallization at 0 °C (THF)$_x$Yb[B$_3$H$_8$]$_2$ was removed from solution. ^{11}B NMR spectrum: in THF-d_8, −26.6 ppm (nonet, J = 33 Hz); in CH_3CN, −29.5 ppm (nonet, J = 33). ^{1}H NMR in CD_3CN: 0.0 ppm (decet, J = 33 Hz).

Preparation of B$_4$H$_{10}$. A 100-mg (1.27-mmol) sample of K[B$_3$H$_8$] was placed in a 50-mL flask with a Teflon stir bar. The flask was evacuated, and 1.3 mmol of BCl_3 (measured as a gas) was condensed into the flask. The reaction was allowed to proceed at −78 °C for 90 min and then warmed to room temperature for an additional 20 min. The reaction mixture was a white slurry. Volatile materials were passed through traps maintained at −98, −140, and −196 °C. A yield of 0.52 mmol of B_4H_{10} (55% based on [B$_3$H$_8$]$^-$ boron) was collected in the −140 °C trap. ^{11}B NMR spectrum in benzene-d_6: −7.58 (triplet, J = 132 Hz), −42.4 ppm (doublet, J = 135 Hz). Both peaks decoupled to singlets. An identical procedure was performed on 0.103 g (1.3 mmol) of K[B$_3$H$_8$] using 1.3 mmol of BF_3, affording 0.50 mmol of B_4H_{10} (51% yield).

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Intramolecular Carbonylation of Ni(S$_2$COR′)$_2$ in Fused PR$_3$. An Improved Preparation of Ni(CO)$_2$(PR$_3$)$_2$

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The ability of fused tertiary arylphosphines to participate in reduction reactions has permitted us to develop a new synthetic pathway to dicarbonylbis(tertiary phosphine)nickel(0) complexes from bis(alkyl xanthato)nickel(II) compounds (alkyl xanthate = *O*-alkyl dithiocarbonate). Depending on the phosphine and the alkyl xanthate used, different yields are achieved.

Several methods of preparation of Ni(CO)$_2$(PR$_3$)$_2$ complexes, all of them using carbon monoxide or highly toxic volatile carbonyls, are described in the literature. Thus the direct reaction between Ni(CO)$_4$ and the phosphine is still by far the most important synthetic method.[1,2]

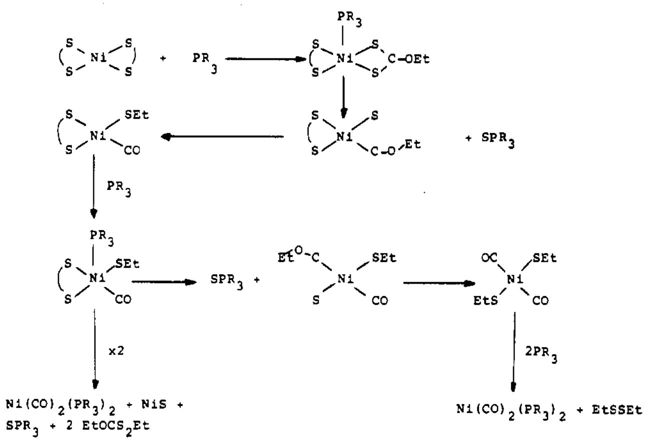
The reductive carbonylation of NiX$_2$(PR$_3$)$_2$ (X = halide) to give Ni(CO)$_2$(PR$_3$)$_2$ has also been carried out by using several reducing agents or by reaction with metal carbonyls or metal carbonyl anions.[2-5] The decarbonylation of methanol occurs in the reaction of PPh$_3$ and Ni(cod)$_2$ in the presence of a diene.[2,6] More recently, the partial formation of Ni(CO)$_4$, when the reaction of Ni(S$_2$COR′)$_2$ with amines was carried out in the presence of CO, was proved.[7]

Table I. Reaction Conditions and Yields

Ni(S$_2$COR′)$_2$ R′	PR$_3$ R	molar ratio PR$_3$/Ni	temp, °C	reacn time, h	yield, %[a]
Et	Ph	6	150–140	1	50
Et	Ph	3	150–120	0.7	30
Et	*p*-$CH_3C_6H_4$	4	150–140	1	4.2
Cy	Ph	6	170–160	1	15
Cy	*p*-$CH_3C_6H_4$	4	170–160	1	trace

[a] Ni(CO)$_2$(PR$_3$)$_2$ relative to Ni(S$_2$COR′)$_2$.

Scheme I. Proposed Mechanism for the Formation of Ni(CO)$_2$(PR$_3$)$_2$



We have previously studied the reactivity of tertiary phosphines toward Ni(S$_2$COR′)$_2$ (R′ = Et, C_6H_{11} (Cy)) compounds in several solvents to give mixed complexes. Under the reported conditions, no reaction was observed with PPh$_3$, but with Ph$_2$PC$_2$H$_4$PPh$_2$ (dppe), an adduct formation reaction or rupture of the O–R′ bond occurred to give dithiocarbonate complexes.[8] In the attempt to isolate derivatives of the PPh$_3$, the reaction was carried out in the fused phosphine. No adducts were isolated in the described reactions; instead, zerovalent nickel complexes were obtained.

As described below, the reaction occurs with formation of Ni(CO)$_2$(PPh$_3$)$_2$ in up to 50% yield, the best results being obtained when ethyl xanthate(1−) and triphenylphosphine are used. Table I shows the reaction conditions and the results obtained. Along with the main product, variable quantities of SPPh$_3$ are recovered. The reaction also produces a black amorphous residue that is analyzed to be a nickel sulfide. The analytical data are variable, depending on the conditions employed in the reaction, but all of them suggest the formation of a nonstoichiometric species $Ni_{1-x}S$ ($0 \le x \le 0.2$).

The organic products of this reaction condensed as colorless drops of liquid in the cooler parts of a Schlenk flask. They were collected, separated by alumina chromatography, and identified by comparison of their ^{1}H NMR spectra with those of authentic samples. From the mixtures we have been able to identify EtSEt (5%), EtSSEt (15%), and EtOCSSEt (30%). In some cases, we could also identify traces of phosphine adducts, similar to those previously reported by us,[8] as shown by the ν(COR) bands shifted to lower frequencies in the IR spectrum. A possible mechanism (Scheme I) would include the initial formation of a pentacoordinate phosphine adduct, followed by sulfur abstraction with liberation of SPPh$_3$.

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