$[MnS_2P(OC_6H_5)_2(CO)_4]$ (cyclohexane solution) shows bands at 2100 (m), 2026 (s), 2006 (s), and 1963 (s) cm^{-1} in the frequency range and pattern expected for a simple, chelated tetracarbonylmanganese complex.[4,5,18] However, although low-resolution spectra appear normal, more carbonyl stretching bands than expected for the simple complexes are found in the high-resolution spectra of $[MnS_2P(OC_2H_5)_2(CO)_4]$ (dichloromethane solution): 2098 (w), 2028 (s), 2021 (m, sh), 2000 (m), 1957 (m, sh), and 1944 (s) cm^{-1}; $[MnS_2P(C_6H_5)_2(CO)_4]$ (dichloromethane solution): 2096 (w), 2025 (s), 2020 (m, sh), 2000 (m), 1953 (m), and 1944 (m, sh) cm^{-1}; and $[MnOSP(OC_2H_5)_2(CO)_4]$ (dichloromethane solution): 2096 (w), 2027 (s), 2004 (m, sh), 1948 (s), and 1920 (m, sh) cm^{-1}. The P–S frequencies of our compounds, *e.g.*, $[MnS_2P(OC_6H_5)_2(CO)_4]$ (broad, medium peaks in Nujol mull): 657, 644, and 535 cm^{-1}, are near those of other dialkyldithiophosphatometal complexes.[19,20]

It appears from the infrared and electronic absorption spectra of our complexes that the bonding properties of the $[(RO)_2PS_2]^-$ group resemble those of the $[(C_2H_5)_2NCS_2]^-$ [4] and $[C_6H_5CS_2]^-$ [5] groups. However, the extinction coefficient (800) at the long-wavelength maximum of $[MnS_2P(OC_6H_5)_2(CO)_4]$ is much closer to those of $[MnBr(CO)_4L]$ complexes (340–730)[10] than to that of $[Mn(C_6H_5CS_2)(CO)_4]$ (6900).[5] Replacement of carbon by phosphorus has only slightly affected the π-bonding ability of the sulfur atoms.

In analogy to the reactions between $[MnBr(CO)_4L]$ and other ligands to give $[MnBr(CO)_3LL']$ species,[10–12] reaction occurs readily between $[MnS_2P(OC_6H_5)_2(CO)_4]$ and Lewis bases to form $[MnS_2P(OC_6H_5)_2(CO)_3L]$ complexes. Only in the case of L = tributylphosphine have we found more than traces of the dicarbonyl complex $[MnS_2P(OC_6H_5)_2(CO)_2L_2]$. Even at higher temperatures for longer times with large excesses of the other ligands, the monosubstituted complexes remain the main products.

The reactions are easily followed by infrared spectroscopy and tentative assignments of structure have been made by analogy with previous work,[9–15,18] although the purported *cis*-phosphite complexes show more carbonyl stretching bands than expected. The following carbonyl stretching bands have been observed for the species *cis*-$[MnS_2P(OC_6H_5)_2(CO)_3L]$ (cyclohexane solution), where $L = P(OC_6H_5)_3$: 2045 (s), 1987 (s), 1973 (s), 1953 (m), and 1938 (s) cm^{-1}; $L = P(OC_2H_5)_3$: 2040 (s), 1972 (s), 1963 (s), 1927 (m), and 1888 (m) cm^{-1}; $L = P(C_4H_9)_3$: 2028 (s), 1945 (s), and 1914 (s) cm^{-1}; $L = C_5H_4N$: 2033 (s), 1944 (s), and 1924 (s) cm^{-1}; $L = C_{10}H_8N_2$ (dichloromethane solution): 2032 (s), 1940 (s, sh), and 1930 (s) cm^{-1}. The following bands have been observed (cyclohexane solution) for *trans*-$[MnS_2P(OC_6H_5)_2(CO)_3P(OC_6H_5)_3]$: 2045 (w), 1974 (s), and 1908 (s) cm^{-1}; for *trans*-$[MnS_2P(OC_6H_5)_2(CO)_3P(OC_2H_5)_3]$: 2040 (w), 1963 (s), and 1883 (s) cm^{-1}; for *cis*-$\{MnS_2P(OC_6H_5)_2(CO)_2[P(C_4H_9)_3]_2\}$: 1923 (s) and 1850 (s) cm^{-1}.

A mixture of *cis* and *trans* isomers was invariably formed with triphenyl phosphite or triethyl phosphite as ligand, low temperatures (0°) favoring the *cis* isomer slightly. No major solvent effects were noted. Crystallization gave fractions enriched in one isomer or the other, so that assignments of structure could be made. Heating of *cis*-$[MnS_2P(OC_6H_5)_2(CO)_3P(OC_6H_5)_3]$ for 6 hr at 80° in cyclohexane solution gave some decomposition, but only slight conversion to the *trans* isomer. Pyridine or α,α'-bipyridyl gave exclusively the *cis* isomer. The displacement of only 1 mole of carbon monoxide by the normally bidentate ligand α,α'-bipyridyl may be explained as involving displacement also of one of the sulfur atoms, so that the $[(C_6H_5O)_2PS_2]$ group functions only as a monodentate ligand. An analogous situation has been reported in the case of the reaction between α,α'-bipyridyl and hexafluoroacetylacetonatotetracarbonylmanganese.[15] The difficulty in preparing $[MnX(CO)_3L_2]$ complexes with triphenylphosphine as ligand has been noted before.[12,14]

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[18] F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964), and references cited therein.

[19] J. Rockett, *J. Appl. Spectry.*, **16**, 39 (1962).

[20] R. A. Chittenden and L. C. Thomas, *Spectrochim. Acta* **20**, 1679 (1964).

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Proton Exchange in a Coordinated Acetylacetonate Ligand

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The exchange of the acidic protons of coordinated ligands (*e.g.*, amine protons) is a well-documented phenomenon[1] and recently Williams and Busch have shown that coordination may lead to the labilization of the less acidic protons of coordinated ligands, such as the α-methylene protons of glycine.[2] The proton-exchange reactions of the coordinated acetylacetonate ligand in the ion $Co(en)_2(acac)^{2+}$ described in this note also show the marked effect which coordination may have upon the reactivity of an organic molecule. The exchange of the protons of the free ligand may be accomplished in basic solution, with the protons at the γ carbon exchanging most readily;[3] however, in

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[1] J. W. Palmer and F. Basolo, *J. Phys. Chem.*, **64**, 778 (1960); B. P. Block and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **73**, 4722 (1951); R. G. Pearson and F. Basolo, *ibid.*, **78**, 4878 (1956); F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, pp 129, 386, 394.

[2] D. H. Williams amd D. H. Busch, *J. Am. Chem. Soc.*, **87**, 4644 (1965).

[3] (a) R. Klar, *Z. Physik. Chem.*, **326**, 335 (1934); *Chem. Abstr.*, **28**, 7123 (1934); (b) A. Murray, III, and D. L. Williams "Organic Synthesis with Isotopes," Interscience Publishers, Inc., New York, N. Y., 1958, Part II, p 1604; (c) R. G. Pearson and E. A. Mayerle, *J. Am. Chem. Soc.*, **73**, 926 (1951).

the complex discussed here, proton exchange in basic D_2O leads to selective exchange of the methyl protons, while exchange in acidic D_2O yields a complex deuterated at the γ carbon of the β-diketonate ligand. It was of interest to note that cleavage[3c] of the free ligand occurs faster than exchange of the methyl groups of the free ligand in the highly basic D_2O media.

Experimental Section

Materials.—$[Co(en)_2(acac)]I_2$ was prepared as described in the literature[4] and the nitrate salt obtained by metathesis with $AgNO_3$. Deuterium oxide (99.83 mole %) was obtained from Bio-Rad Laboratories. Other compounds were prepared by methods in the literature or were commercial reagent grade materials. All materials gave satisfactory analyses.

Exchange Reactions.—Exchange of the methyl protons was carried out in D_2O–NaOH solutions. In a typical reaction, 0.113 g (2.8 mmoles) of NaOH was dissolved in 3 ml of D_2O and 0.083 g (0.18 mmole) of $[Co(en)_2(acac)](NO_3)_2$ was added. After standing 20 min at room temperature, the solution was filtered from decomposition products (presumably $Co_2O_3 \cdot nH_2O$) and excess KI was added to precipitate the product. The solid was filtered, washed with acetone, and air dried. Exchange of the protons at the γ carbon of the β-diketonate ligand was carried out in an analogous manner in concentrated D_3PO_4–D_2O solutions.

Spectral Measurements.—Proton magnetic resonance spectra were recorded in D_2O and H_2O solution on a Varian A-60 nuclear magnetic resonance spectrometer. Infrared spectra were obtained in Nujol or Kel-F mulls with a Perkin-Elmer Model 337 spectrophotometer. Visible and ultraviolet spectra were measured in 10-mm path length quartz cells with a Beckman DB spectrophotometer.

Results

Solutions of $[Co(en)_2(acac)](NO_3)_2$ in D_2O exhibit proton resonances at $\delta = 0.90$, 1.54, and 4.53 ppm (measured with respect to the methyl resonance of *t*-butyl alcohol) with integrated intensities 6:8:1, corresponding to the methyl groups of the acetylacetonate group, the methylene protons of the ethylenediamine chelate ring, and the remaining proton at the γ carbon of the acetylacetonate ring, respectively. In neutral or acidic D_2O solutions, the amine protons give two broad signals, one at a slightly higher field and one at slightly lower field than the HDO line, which disappears upon exchange with the solvent.[5] In addition to the exchange of the amine protons, exchange of the proton at the γ carbon of the acetylacetonate group is suggested by the disappearance of this signal in acidic D_2O solutions. A similar observation has been made by Collman.[6] In concentrated D_3PO_4–D_2O solutions, the exchange of the proton at the γ carbon occurs in the time required to prepare a sample for pmr measurement; however, only small amounts of deuterium are introduced into the amine positions. In basic D_2O solutions, on the contrary, rapid exchange of the amine protons is followed by a slower exchange of the methyl group of the acetylacetonate ligand as evidenced by the loss of the signal at $\delta = 0.9$ ppm with the retention of the resonance at $\delta = 1.54$ and 4.53 ppm. The conditions used in the basic exchange reactions lead to the cleavage of free acetylacetone to yield deuterated acetone and undeuterated acetate anion. The integrated area of the parent peak plus twice the area of the acetate peak remained essentially constant indicating that under these drastic conditions the exchange of the methyl groups of the free ligand is a slow process. The lack of a signal in the regions expected for protons attached to the γ carbon suggests that exchange occurs rapidly at this position. The lack of exchange of the methyl groups may likely be ascribed to the fact that in these extremely basic solutions the free ligand is present as the enolate anion necessitating the formation of a dianion for exchange to occur at the methyl groups.

In addition to the exchange reactions, evidence for some decomposition is observed in the concentrated base solutions; therefore, the reaction products were isolated as described above and their ultraviolet and infrared spectra were compared to samples of $[Co(en)_2(acac)]I_2$. The position of absorption bands in the visible and ultraviolet were identical in the exchanged and unexchanged $[Co(en)_2(acac)]I_2$. In addition, $[Co(en)_2(acac)]I_2$ was found to be the product of similar treatment of the starting material with H_2O–NaOH solutions. As discussed below, the infrared spectra are in agreement with the selective exchange of the protons of the β-diketonate ligand suggested by the proton magnetic resonance spectra.

The product of acid-catalyzed exchange shows a new infrared absorption band at 925 cm^{-1}, the region in which $\geqslant$C–D[7] deformations are expected.[8] The absence of this absorption in the base-catalyzed exchange is a further indication of the selectivity of these exchange reactions. A weak absorption at 2140 cm^{-1} is assigned to the $\geqslant$C–D stretching frequency, the absence of this band in the product of base-catalyzed exchange being less certain as this is the region in which the more intense $-ND_2$ stretching modes occur. Boucher and Bailar[4] have discussed the deuterium exchange of the labile protons of this complex in neutral D_2O. They have assigned an absorption at 935 cm^{-1} (also observed in this work) to the $\geqslant$C–D deformation; however, the proton magnetic resonance spectra of neutral solutions of $Co(en)_2(acac)^{2+}$ suggest that the exchange of the proton at the γ carbon is quite slow under these conditions and that the band at 935 cm^{-1} is associated with an $-ND_2$ wagging mode shifted from $\sim$1300 cm^{-1} for $-NH_2$.[9] The relative inertness of the γ position of coordinated acetylacetonate ligands to exchange in neutral media has been observed previously.[8]

The product of base-catalyzed exchange shows shifts in infrared bands which support exchange of the methyl groups suggested by the pmr spectra. The infrared shifts are summarized in Table I, the assignments being made by comparison to the assignments of Nakamoto, *et al.*, for $Co(acac)_3$.[10] In general, those bands assigned

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[4] L. J. Boucher and J. C. Bailar, Jr., *Inorg. Chem.*, **3**, 589 (1964).

[5] P. Clifton and L. Pratt, *Proc. Chem. Soc.*, 339 (1963).

[6] J. P. Collman in Advances in Chemistry Series, No. 49, R. F. Gould, Ed., American Chemical Society, Washington, D. C., 1965, p 171.

[7] The symbol $\geqslant$C–H is used to indicate the remaining C–H bond at the central carbon of the acetylacetonate group.

[8] C. Djordjevic, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 4778 (1962).

[9] D. B. Powell and N. Sheppard, *Spectrochim. Acta*, **17**, 68 (1961).

[10] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 216.

TABLE I

INFRARED FREQUENCIES FOR $[Co(en)_2(L)]I_2$

L			
acac	acac-d_1[a]	acac-d_6[a]	Assignment[b]
1520	1480	1520	ν(C–O) + δ(C–H)
1390	1390	(?)	δd(CH_3)
1370	1370	970	δs(CH_3)
1190	925	*c*	δ(C–H)
1030 sh	1030 sh	880	ρ_r(CH_3)
805	665	805	π(C–H)
640	640	620	δ(C–CH_3) + ν(MO)

[a] The symbols acac-d_1 and acac-d_6 correspond to complexes enriched with deuterium at the γ carbon and methyl groups, respectively. [b] The assignments follow the notation of Nakamoto (see ref 10). [c] The region around 1200 cm^{-1} is partially obscured by absorption due to $-ND_2$ groups; however, a shoulder is found at ~1190 cm^{-1}.

to methyl vibrations are shifted while those assigned to >C–H vibrations are left unshifted or only slightly effected.

Discussion

The selectivity of exchange reactions of this complex may be understood in terms of the effect of coordination upon the electronic properties of the β-diketonate ligand. The reactivity of the γ carbon of acetylacetonate ligands toward electrophilic reagents, the position of the >C–H stretching frequency, and other evidence have been cited to support the concept of aromaticity as applied to β-diketonate chelate rings.[11] Within this framework, the acid-catalyzed exchange reaction noted here is likely to be a special case of the more general class of electrophilic substitution reactions in this group of compounds. The general kinetic inertness of Co(III) complexes and the stability of this particular complex to acid hydrolysis conditions[4] suggest that the exchange takes place with the ligand coordinated.

Qualitatively, the rate of exchange of the methyl groups is strongly dependent upon the base concentration, suggesting a mechanism involving the formation of a carbanion intermediate. The stabilization of such an intermediate by delocalization of the charge into the chelate ring might be expected to favor such a reaction whether the mechanism involves a preequilibrium acid–base reaction or the rate-determining attack by base to form an active intermediate. The selectivity of this reaction and particularly the retention of the proton resonance at δ = 4.53 ppm during the exchange reaction strongly suggest that exchange occurs without opening of the chelate ring. Kinetic studies of both the acid- and base-catalyzed reactions have been initiated.

Acknowledgment.—Proton magnetic resonance spectra were obtained with a Varian A-60 nmr spectrometer purchased with matching funds from the National Science Foundation under Grant GP-3655. Thanks are due to Mr. John Martin for preparing some of the compounds used in this work and to Miss Katherine Eggers, who performed the analyses.

CONTRIBUTION FROM THE EVANS AND MCPHERSON CHEMICAL LABORATORIES, THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO

Aluminum–Aluminum Covalent Bonds.
I. Hexamethyltris(dimethylamino)monoborontetraaluminum

BY E. P. SCHRAM

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The treatment of aluminum trimethyl with diborane(4) tetrakisdimethylamide results in the formation of several known compounds; dimethylaminodimethylboron, trimethylboron, dimethylaminodimethylaluminum, and a nonvolatile yellow solid. The yellow solid contains aluminum in an apparent oxidation state of +1.5 and represents the first example of a compound containing Al–Al covalent bonds.

Diborane(4) tetrakisdimethylamide (*ca.* 20 mmoles) was treated with aluminum trimethyl in mole ratios, $B_2[N(CH_3)_2]_4:Al(CH_3)_3$, of *ca.* 1:2 to 1:5. Mole ratios of 1:3 or less yield reaction solutions which are dark red, whereas mole ratios >1:3 result in solution colors varing from pale yellow to dark green. Only mole reactant ratios <1:3 afford trimethylboron, the formation of which is accompanied by an increased yield of $[(CH_3)_2AlN(CH_3)_2]_2$ and a decreased yield of $(CH_3)_2BN(CH_3)_2$. No starting material was recovered for the mole reactant ratio, $B_2[N(CH_3)_2]_4:Al(CH_3)_3$, of 3:8.

Characterization of Volatile Reaction Products

Identification of $(CH_3)_2BN(CH_3)_2$ consisted of vapor tension data comparison with a literature value,[1] infrared spectrum,[2] H^1 nmr spectrum (Table I), and molecular weight determination (calcd: 84.8; found: 85.7). The H^1 nmr spectrum consisted of two peaks of equal area at −0.05 and −2.32 ppm, relative to tetramethylsilane (TMS). Trimethylboron was identified by its vapor tension at −78°, 29 torr,[3] and from its known infrared spectrum.[4] The white crystalline solid, $[(CH_3)_2AlN(CH_3)_2]_2$, was characterized by comparison of its vapor tension and melting point with the literature value,[5] H^1 nmr spectrum (Table I), and infrared spectrum (Table II). The relative molar amounts of $(CH_3)_2BN(CH_3)_2$ and $(CH_3)_2AlN(CH_3)_2$ produced in the reaction were estimated by volume and found to be approximately equal.

Characterization of Hexamethyltris(dimethylamino)monoborontetraaluminum

Treatment of $B_2[N(CH_3)_2]_4$ with $[Al(CH_3)_3]_2$ results in the formation of the volatile species: $[(CH_3)_2AlN(CH_3)_2]_2$, $(CH_3)_2BN(CH_3)_2$, and $(CH_3)_3B$. After re-

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[11] J. P. Collman in Advances in Chemistry Series, No. 37, R. F. Gould, Ed., American Chemical Society, Washington, D. C., 1963, p 78.

(1) G. E. Coates, *J. Chem. Soc.*, 3481 (1950).

(2) J. W. Dawson, P. Fritz, and K. Niedenzu, *J. Organometal. Chem.*, **5**, 13 (1966).

(3) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p 123.

(4) W. J. Lehmann, C. O. Wilson, and I. Shapiro, *J. Chem. Phys.*, **28**, 777 (1958).

(5) N. Davidson and H. C. Brown, *J. Am. Chem. Soc.*, **64**, 316 (1942).