Notes

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A Novel Phosphorus-Centered Heterometallic Cluster

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The reactivity of the silicon–hydrogen bond in a variety of silanes can be exploited in convenient syntheses for several silicon-centered heterometallic clusters. These syntheses, previously described,[1] are more usefully applied to clusters involving the odd-numbered transition metals. The isosteric identity of $H_3SiMn(CO)_5$ and $H_3PCr(CO)_5$ suggested the possibilities of synthesizing phosphorus-centered heterometallic clusters incorporating even-numbered transition metals. Syntheses obviously could be effected in reactions analogous to the reactions of isosteric silanes if the phosphorus–hydrogen bond displayed similar chemical reactivity. Such a possibility is indicated in a reaction reported by Hieber and Winter:[2]

$$2V(CO)_6 + 2PH_3 \rightarrow (CO)_4V \overset{PH_2}{\underset{PH_2}{\diagup\diagdown}} V(CO)_4 + H_2 + 4CO \qquad (1)$$
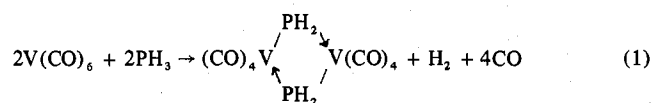
The evolution of hydrogen in this reaction has its parallel in silane chemistry already mentioned.[1]

Results and Discussion

The treatment of a tetrahydrofuran solution of pentacarbonylphosphinochromium, $H_3PCr(CO)_5$, with a deficiency of cobalt octacarbonyl, $Co_2(CO)_8$, results in a steady evolution of a mixture of hydrogen and carbon monoxide. The reaction

$$H_3PCr(CO)_5 + Co_2(CO)_8 \rightarrow HPCrCo_2(CO)_{11} + H_2 + 2CO \qquad (2)$$
$$\text{I}$$
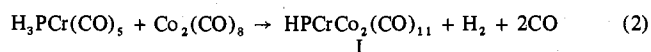
is complete after 60 h at room temperature. The amount of pentacarbonylphosphinochromium remaining after completion is consistent with the equation given. The yield of product I is quantitative. The dark red crystalline solid I is quite soluble in methylene chloride and tetrahydrofuran, yet only sparingly soluble in *n*-hexane. The new compound is indefinitely stable in vacuo at room temperature and does not visibly change upon exposure to air for short periods of time. It is apparently slightly volatile in vacuo at elevated temperatures but decomposes at temperatures in excess of 90 °C as evidenced by the deposition of a metallic mirror on the walls of the reaction vessel. The volatile products of this decomposition have yet to be examined.

It is of interest that the infrared spectrum of this new cluster does not indicate the presence of any bridging carbonyl ligands, especially so since the most closely similar known silicon-centered cluster, μ-pentacarbonylchlorosilyl-μ-carbonylbis(tricarbonyl)cobalt, $Cl[Mn(CO)_5]SiCo_2(CO)_7$, involves such
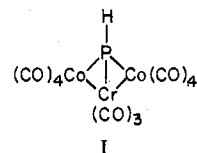
Table I. Mass Spectrum of $HPCrCo_2(CO)_{11}$

Ion	Rel intens	Ion	Rel intens
$HPCrCo_2(CO)_{11}{}^+$	2	$HPCrCo_2(CO)_3{}^+$	1
$PCrCo_2(CO)_{11}{}^+$	13	$PCrCo_2(CO)_3{}^+$	14
$HPCrCo_2(CO)_{10}{}^+$	3	$PCo_2(CO)_4{}^+$	10
$PCrCo_2(CO)_{10}{}^+$	19	$HPCrCo_2(CO)_2{}^+$	3
$HPCrCo_2(CO)_9{}^+$	2	$PCrCo_2(CO)_2{}^+$	31
$PCrCo_2(CO)_9{}^+$	16	$PCrCo_2(CO)^+$	9
$HPCrCo_2(CO)_8{}^+$	2	$PCrCo_2{}^+$	17
$PCrCo_2(CO)_8{}^+$	13	$CrCo_2{}^+$	5
$HPCrCo_2(CO)_7{}^+$	2	$PCo_2{}^+$	24
$PCrCo_2(CO)_7{}^+$	20	$Cr(CO)_3{}^+$	4
$PCo_2(CO)_8{}^+$	3	$PCo(CO)^+$	9
$HPCrCo_2(CO)_6{}^+$	2	$Co(CO)_2{}^+$	9
$PCrCo_2(CO)_6{}^+$	16	$Cr(CO)_2{}^+$	28
$PCo_2(CO)_7{}^+$	4	$HPCo^+$	14
$HPCrCo_2(CO)_5{}^+$	1	$Co(CO)_5{}^+$	28
$PCrCo_2(CO)_5{}^+$	16	$HPCr^+$	50
$PCo_2(CO)_6{}^+$	5	PCr^+	5
$HPCrCo_2(CO)_4{}^+$	2	$Cr(CO)^+$	58
$PCrCo_2(CO)_4{}^+$	17	Co^+	14
$PCo_2(CO)_5{}^+$	8	Cr^+	100

a bridging carbonyl. Apparently, in this silicon-centered cluster more CO ligands also are required for stability.

The fragmentation of I in the mass spectrometer clearly shows the parent ion and fragments resulting from the successive loss of CO ligands without significant loss of the underlying cluster structure. The fragmentation pattern is informative. The family of ions including the parent molecular ion, $HPCrCo_2(CO)_x{}^+$ (where $x = 0\text{--}11$), are observed, but the family of ions where hydrogen is lost, $PCrCo_2(CO)_x$ (where $x = 0\text{--}11$), is approximately four–five times more intense. In this family, formed by successive loss of carbon monoxide ligands, the abundance of each is essentially constant. The cluster, $PCrCo_2{}^+$, is as abundant as the average of all members this family. These facts suggest that the loss of hydrogen from the cluster is relatively facile and that coordinatively unsaturated clusters possess moderate stability. Both of these properties should be useful in catalytic applications.

The phosphorus–hydrogen bond in I has so far proved intractable to further metallic substitution. Treatment of I with an excess of cobalt octacarbonyl and manganese pentacarbonyl hydride under a variety of conditions did not effect further metalation of the phosphorus.

The most probable structure for I in agreement with its infrared, NMR, and mass spectra is[3]

$$(CO)_4Co \overset{\overset{\displaystyle H}{\underset{\displaystyle |}{P}}}{\underset{\underset{\displaystyle (CO)_3}{Cr}}{\diagup\diagdown}} Co(CO)_4$$

$$\text{I}$$

This structure utilizes the electron pairs on each $-Co(CO)_4$ group which usually are "nonbonding". While this is unusual, the mass fragmentation pattern, shown in Table I, furnishes sound support for this proposal. The ions $PCo_2(CO)_8{}^+$ and $PCo_2(CO)_7{}^+$ appear in reasonable intensities and only those ions, containing chromium in the absence of cobalt, possessing fewer than three CO ligands, $Cr(CO)_3{}^+$, $Cr(CO)_2{}^+$, and $Cr(CO)^+$, are observed.

Experimental Section

All reactions reported here were carried out in the absence of air and moisture, using standard vacuum apparatus and procedures, unless otherwise noted. Proton NMR data were obtained using the Varian HA 100 spectrometer, infared spectra on the Perkin-Elmer 180 spectrometer, and mass spectra on the Hitachi RMU-6L spectrometer. All reactants and solvents were cryogenically degassed before use.

Analyses not performed in our laboratory were reported to us by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Reagents. Cobalt octacarbonyl, $Co_2(CO)_8$, was used as obtained from Strem Chemicals, Danvers, Mass. When not in use it was stored at -79 °C under a nitrogen atmosphere.

n-**Hexane,** purchased from Fisher Scientific, Medford, Mass., was distilled from lithium aluminum hydride and purified by fractional condensation through traps at -45, -63, and -196 °C until the material retained at -63 °C exhibited a vapor pressure of 45 mm at 0 °C.

Iodine, from Merck and Co., Inc., Rahway, N.J., was vacuum sublimed before use.

Methylene chloride, CH_2Cl_2, from Mallinckrodt Chemicals, St. Louis, Mo., was dried by distillation from phosphorus pentoxide and purified by fractional condensation through traps at -63, -98, and -196 °C. The fraction retained at -98 °C which exhibited a vapor pressure of 40 mm at -23 °C was assumed to be pure CH_2Cl_2.

Pentacarbonylphosphinochromium, $H_3PCr(CO)_5$, was prepared by the method of Klabunde et al.[4] The physical properties agreed with those in the literature.[4,5]

Synthesis of $HPCrCo_2(CO)_{11}$. In a typical preparation, 0.837 g (3.70 mmol) of $H_3PCr(CO)_5$ and 0.901 g (2.64 mmol) of $Co_2(CO)_8$ were placed in a 50-mL round-bottom flask fitted with several break-off seals and a magnetic stirring bar. These operations were effected in a dry nitrogen atmosphere box. This reaction flask then was attached to the vacuum apparatus and evacuated. The flask was cooled to -79 °C and freshly distilled dry tetrahydrofuran was condensed onto the reactants. When the reaction flask was allowed to warm to room temperature, an immediate reaction ensued as evidenced by a slow but steady evolution of a noncondensable gas. Periodically, during the next 60 h, the reaction vessel was cooled to -196 °C and the noncondensable product gas removed. After each removal the vessel was allowed to warm to and remain at room temperature with vigorous stirring. When no further noncondensable gas was formed the stirring was discontinued. During the 60-h reaction period the solution in the vessel darkened from red to dark blood red. The total gas collected during the 60 h of reaction consisted of a mixture of 2.66 mmol of hydrogen gas and 5.26 mmol of carbon monoxide.

Removal of the tetrahydrofuran from the reaction vessel left a dark blood red crystalline solid. The reaction vessel then was heated to 50 °C and material volatile at the temperature removed. This material was separated by fractional condensation techniques into 0.242 g (1.07 mmol) of $H_3PCr(CO)_5$ and a small amount of tetrahydrofuran. Any unreacted $Co_2(CO)_8$ should also have been removed in this step.

Thus, 2.64 mmol of $Co_2(CO)_8$ and 2.63 mmol of $H_3PCr(CO)_5$ (3.70–1.07) were consumed in the reaction. From these data and the amount of hydrogen and carbon monoxide produced, the empirical composition of the crystalline product is $H_{0.97}P_{1.00}Cr_{2.00}(CO)_{11.03}$.

The product is evidently homogeneous since all of the residue could be dissolved in either methylene chloride or hexane.

Analysis of the dark red solid for carbon monoxide content, using the method of Hallock[6] involving oxidation by iodine in pyridine solution, gave a carbon monoxide count of 10.84 compared with 11.00 for $HPCrCo_2(CO)_{11}$.

Total elemental analysis by an outside laboratory gave results in good agreement with the empirical formula. Anal. Calcd: H, 0.20; P, 6.08; Cr, 10.2; Co, 23.2; C, 25.9; O, 34.5. Found: H, 0.30; P, 5.30; Cr, 8.0; Co, 25.2; C, 26.5; O, 34.7.

The mass spectrum, obtained using a direct solids inlet and an ionizing potential of 70 eV, is shown in Table I. The molecular ion at a mass number of 510 established $HPCrCo_2(CO)_{11}$ as the molecular formula.

A methylene chloride solution gave infared absorptions at 2110 (w), 2069 (sh), 2030 (sh), 1974 (m), and 1952 (s) cm^{-1}.

The proton NMR spectrum of a CCl_3D solution consisted of a doublet centered at τ 5.85 with a $J(P–H) = 276$ Hz.

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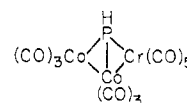
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Photochemistry of Complex Ions. 16. $Cr(NH_3)_5F^{2+}$

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The ligand field photochemistry of chromium(III) ammines has been extensively studied,[1] particularly with respect to supporting, disproving, modifying, or explaining Adamson's photolysis rules.[1] Early exceptions to these rules were *trans*-$Cr(cyclam)Cl_2^+$[2] (being nearly photoinert) and *trans*-$Cr(en)_2F_2^+$.[3] The photoproduct in this last case is *trans*-$Cr(en)(enH)(H_2O)F_2^{2+}$ rather than *cis*-$Cr(en)_2$-$(H_2O)F^{2+}$, as expected in analogy to the behavior of *trans*-$Cr(en)_2Cl_2^+$.[4] However, the lowest quartet excited state for *trans*-$Cr(en)_2F_2^+$ is σ antibonding in $d_{x^2-y^2}$ rather than in d_{z^2},[5] the more usual for chromium(III) ammines. This assignment has provided a basis for explaining the anomalous photochemistry.[3,6,7]

It seemed surprising that the photochemistry of $Cr(NH_3)_5F^{2+}$ had not been studied in view of the special behavior of fluoride as a ligand and the extensive investigations of other members of the $Cr(NH_3)_5X^{2+}$ series.[1] The present investigation was undertaken to remedy this omission. An additional point of interest was whether the photochemistry of $Cr(NH_3)_5F^{2+}$ might show some informative pH behavior. Since fluoride is both an atomic ligand and the anion of a weak acid, there was the possibility of acid-catalyzed photochemistry. The thermal substitution chemistry is predominantly one of fluoride aquation ($k = 2.46 \times 10^{-7}$ s^{-1} at 25 °C[8]) and is indeed acid catalyzed.

Experimental Section

Preparations. Aquopentaamminechromium(III) Nitrate. The preparation was by the method of Mori[9] and provided the starting material for the next preparation.

Fluoropentaamminechromium(III) Perchlorate. This complex was prepared from the aquopentaammine by a literature procedure.[10] The salt was recrystallized twice from a saturated solution by the dropwise addition of a filtered saturated sodium perchlorate solution. The product was then recrystallized by cooling a saturated solution to 5 °C. The needle-shaped crystals were washed with ethanol and ether, then air-dried. The final yield was 18%. The product contained less than 0.1% of free fluoride and the absorption spectrum in 0.01 M perchloric acid was in excellent agreement with the literature[10] (band maximum in nm (extinction coefficient, M^{-1} cm^{-1})): 502 (41.7), 367 (21.0). Anal. Calcd for $[Cr(NH_3)_5F](ClO_4)_2$: Cr, 14.65; F, 5.35. Found: Cr, 14.95; F, 5.18.

Analytical Methods. Free ammonia was determined by the indophenol spectrophotometric method,[11] which was calibrated against a known ammonium chloride solution. In order to correct for pH effects, calibration curves were prepared for each pH used.

Photoreleased fluoride was measured with an Orion Model 96-09 combination fluoride electrode connected to a Beckman Model 1019 research pH meter. In order to obtain stable millivolt readings, it