

precision in this study ($\sim \pm 0.01 \text{ \AA}$ and $\pm 0.5^\circ$), the two molecules are identical; one of the molecules is shown in Figure 1, and the lattice arrangement is shown in a stereoview in Figure 2. The pyrrole rings are planar (maximum deviation = 0.005 \AA) and perpendicular (tilt angle = $< 1^\circ$) to the rotation cone created by the $\text{Mn}(\text{CO})_3$ pedestal. The molecule possesses near mirror-plane symmetry defined by the atoms N(1), Mn(1), C(8), O(8), and the midpoint of the C(3)–C(4) bond. The recently re-determined structure¹¹ of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ showed only a narrow range of Mn–C(ring) distances: 2.145 (2)–2.155 (2) \AA . We find for the 3,4-dimethylpyrrolyl complex a much greater range 2.12 (1)–2.20 (1) \AA (both sets with rigid-body librational corrections). The values at the short end of the range are the Mn(1)–N(1), Mn(1)–C(2), and Mn(1)–C(5) distances, and the long distances are the Mn(1)–C(3) and Mn(1)–C(4) bonds. This pattern represents some slippage¹² of the ring centroid toward N(1) by 0.060 \AA from the intersection of the ring and the Mn–ring perpendicular vector.

All previously reported structures of $(\eta^5\text{-pyrrolyl})\text{Mn}(\text{CO})_3$ complexes have contained N-coordinated metallic groups.¹³ Where error limits have been low enough to permit at least a 0.03-\AA discrimination, the same ring slippage is seen, although to a lesser extent. Since none of the previously determined $(\eta^5\text{-pyrrolyl})\text{Mn}(\text{CO})_3$ complex structures were corrected for librational effects, it is difficult to make precise comparisons.

The C–N ring bonds, 1.37 \AA (average), are shorter than the C–C ring bonds, 1.41 \AA (average). Within the estimated standard deviations of these parameters (and for the previously reported N-coordinated pyrrole complexes) no indication exists for either diene or allyl–ene localization within the ring.

The $\text{Mn}(\text{CO})_3$ group conforms closely to that found in $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$.¹¹ Unfortunately, we are unable to compare the X-ray structure of **2** with that of **3** because it formed an oil.

The results of this investigation show the subtlety of factors that affect rates of ligand substitution of transition-metal organometallic complexes. Work in progress on such factors will be reported in more detail later.

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Supplementary Material Available: Tables atomic coordinates, bond distances, bond angles, anisotropic temperature factors, and hydrogen atom coordinates (5 pages); a listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

A New Method for the Preparation of Monofluorophosphane Complexes. Isolation of $[(\text{CO})_5\text{CrP}(\text{NET}_2\text{Me})\text{Et}_2][\text{BF}_4]^\dagger$

Mathias Höfler,* Martin Stubenrauch, and Elisabeth Richarz

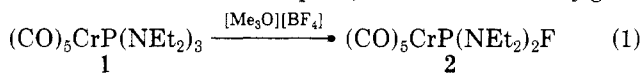
Institut für Anorganische Chemie der Universität
D-5000 Köln 41, West Germany

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Summary: Complexed aminophosphane ligands undergo a single NR_2/F exchange on reaction with $[\text{Me}_3\text{O}][\text{BF}_4]$; for instance, $(\text{CO})_5\text{CrP}(\text{NET}_2)_3$ yields $(\text{CO})_5\text{CrPF}(\text{NET}_2)_2$. With $(\text{CO})_5\text{CrPEt}_2\text{NET}_2$, however, the ammoniophosphane complex $[(\text{CO})_5\text{CrP}(\text{NET}_2\text{Me})\text{Et}_2][\text{BF}_4]$ is formed.

The first step in the acid cleavage of complexed aminophosphanes consists in the protonation of the nitrogen, thereby forming ammoniophosphane complexes.² There have been attempts to isolate these intermediates, but only products contaminated by ammonium salts^{3,4} could be obtained. They have been characterized by NMR spectroscopy in one case.³ Quite recently, the protonation of a complexed tricyclic aminophosphane led to an analytically pure substance.⁵ It is reasonable that the reaction stops at this stage because of the great stability of the cyclic ligand and that cleavage of the P–N bond does not occur as a consequence. The protonated complex behaves as a strong acid and reacts with bases to yield the starting complex.

These results suggest that the reason why the initially formed ammoniophosphane complexes defied isolation, or even detection in most cases, lies in their great tendency to undergo cleavage of the P–N bond. For the preparation of stable ammoniophosphane complexes large anions with negligible nucleophilicity should therefore be used. Furthermore, we expected an additional stabilization by alkylation instead of protonation. As a consequence of these considerations, we examined the reactions of aminophosphane complexes with oxonium salts. Assuming that the stability of the desired compounds is enhanced with increasing electron density at the phosphorus atom, we started with **1**. To our surprise, we isolated **2** in very good



yield. The formation of **2** parallels most reactions with

(10) Crystallographic data: $\text{C}_9\text{H}_9\text{MnNO}_3$, monoclinic, $P2_1/n$, $a = 6.578$ (2) \AA , $b = 29.285$ (7) \AA , $c = 10.910$ (3) \AA , $\beta = 99.88$ (2)°, $V = 2070.3$ (7) \AA^3 , $Z = 8$, $D(\text{calcd}) = 1.495 \text{ g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 12.0 \text{ cm}^{-1}$, $T = 293 \text{ K}$. All crystals examined showed evidence of a progressive, nondestructive phase transformation; jagged, stepped boundaries between phases moved with time, suggesting a defect or impurity nucleated process. The specimen chosen for data collection ($0.28 \times 0.32 \times 0.44 \text{ mm}$), grown from pentane, was cleaved from a larger specimen and appeared to be a single phase. The crystal was multiply layered with epoxy cement to prevent sublimation. Intensity data were collected (Nicolet R3m) rapidly ($6\text{--}20^\circ \text{ min}^{-1}$) to the limit of observation ($2\theta = 45^\circ$). Decay in I was less than 2%. Merging 2938 data yielded 2703 unique data ($R_{\text{int}} = 2.6\%$) of which 1242 with $F_o \geq 3\sigma(F_o)$ were considered observed. The structure was solved by direct methods and completed by difference Fourier syntheses. The asymmetric unit consists of two molecules of $(\eta^5\text{-C}_4(\text{CH}_3)_2\text{H}_2\text{N})\text{Mn}(\text{CO})_3$. Due to the small fraction of observed data, the carbon atoms of the rings and methyl groups were isotropically refined; the remaining non-hydrogen atoms were anisotropically refined. Hydrogen atoms were treated as idealized, isotropic contributions: C–H = 0.96 \AA , $R_F = 5.45\%$, $R_wF = 6.33\%$, GOF = 1.21, $\Delta/\sigma = 0.06$, $\Delta(\rho) = 0.41 \text{ e \AA}^{-3}$, and $N_o/N_v = 6.4$. SHELXTL (5.1) software was used for all calculations (Nicolet Corp., Madison, WI).

(11) Fitzpatrick, P. J.; Page, Y. L.; Sedman, J.; Butler, I. S. *Inorg. Chem.* **1981**, *20*, 2852.

(12) Faller, J. W.; Crabtree, R. H.; Habib, A. *Organometallics* **1985**, *4*, 929–935.

(13) Pyshnograeva, N. I.; Setkina, V. N.; Andianov, V. G.; Struchkov, Yu. T.; Kursanov, D. N. *J. Organomet. Chem.* **1977**, *128*, 381; **1978**, *157*, 431; **1980**, *186*, 331; **1981**, *206*, 177; **1981**, *209*, 169.

(1) Part 7 of the series: Exchange Reactions at Complexed Ligands of Elements of Group Vb. Part 6: Höfler, M.; Hausmann, H.; Schneider, A. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1559.

(2) Höfler, M.; Schnitzler, M. *Chem. Ber.* **1972**, *105*, 1133.

(3) Teich, W.; Kruck, Th., unpublished results. See: Teich, W. *Dissertation Universität zu Köln*, 1981.

(4) Maisch, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 61.

(5) Febvay, J.; Casabianca, F.; Riess, J. G. *J. Am. Chem. Soc.* **1984**, *106*, 7985.

Table I. ^1H NMR Spectra of $(\text{CO})_5\text{CrPEt}_2\text{NET}_2$ (**3**) and $[(\text{CO})_5\text{CrP}(\text{NET}_2\text{Me})\text{Et}_2][\text{BF}_4]$ (**4**) (in CH_2Cl_2)

	$(\text{CO})_5\text{CrP}(\text{CH}_2\text{CH}_2\text{CH}_3)_2$ $\text{N}(\text{CH}_2\text{CH}_2\text{CH}_3)_2$	$(\text{CO})_5\text{CrP}(\text{CH}_2\text{CH}_2\text{CH}_3)_2$ $\text{N}(\text{CH}_2\text{CH}_2\text{CH}_3)_2$ $\text{H}'_3\text{C}$ H^{d_2}
δ_{H_a}	2.02	2.67
δ_{H_b}	1.74	2.39
δ_{H_c}	1.11	1.37
δ_{H_d}	3.04	3.37 (d ₁), 3.18 (d ₂)
δ_{H_e}	1.15	1.57
δ_{H_f}		3.24
$^2J_{\text{ab}}$	14.6	15.1
$^3J_{\text{ac}}$	7.3	7.6
$^3J_{\text{bc}}$	7.3	7.7
$^3J_{\text{de}}$	6.8	7.3
$^2J_{\text{H}_a\text{P}}$	9.7	9.4
$^2J_{\text{H}_b\text{P}}$	0.2	0.5
$^3J_{\text{H}_c\text{P}}$	10.8	17.7
$^3J_{\text{H}_d\text{P}}$	9.1	a

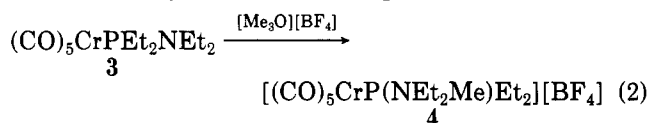
^a Because of the large quadrupole effect of the quarternary nitrogen, the resolution is not high enough to allow the evaluation of the $^3J_{\text{H}_{d_1}\text{P}}$, $^3J_{\text{H}_{d_2}\text{P}}$, $^3J_{\text{H}_c\text{P}}$, $^3J_{\text{H}_{d_1}\text{Me}}$, $^3J_{\text{H}_{d_2}\text{Me}}$, and $^3J_{\text{H}_{d_1}\text{H}_{d_2}}$ coupling constants.

hydrogen halides insofar as it is not possible to isolate any intermediate complexes.

Reaction 1 is very convenient for monofluorination, since even with a large excess of $[\text{Me}_3\text{O}][\text{BF}_4]$ only one of the three NET_2 groups is exchanged. This proved also to be the case with other compounds such as $(\text{CO})_5\text{CrPPh}(\text{NET}_2)_2$ and $(\text{CO})_5\text{CrP}(-\text{OC}_2\text{H}_4\text{O}-)\text{NET}_2$, whereby $(\text{CO})_5\text{CrPPh}(\text{NET}_2)\text{F}$ and $(\text{CO})_5\text{CrP}(-\text{OC}_2\text{H}_4\text{O}-)\text{F}$ were obtained in 82% and 32% yields, respectively.

If $(\text{CO})_5\text{CrPPh}_2\text{NET}_2$ is used as starting material, besides $(\text{CO})_5\text{CrPPh}_2\text{F}$ (57%), *cis*-/*trans*- $(\text{CO})_4\text{Cr}(\text{PPh}_2\text{F})_2$ (19%) is isolated. The latter compound stems from CO substitution. The ratio of mono- to disubstitution depends on the solvent used for the reaction; in CH_2Cl_2 it is 3:1 and in 1,2-dimethoxyethane, 1:1. In both cases the *cis*/*trans* ratio is an almost constant 3:1.

When substituents on the phosphorus were changed, we were able to synthesize **4** starting from **3**. **4** is the first



complex with a (trialkylammonio)phosphane ligand. Alkylation of the lone electron pair of the nitrogen atom of **3** results in smaller donor/larger acceptor capacities of the phosphane ligand. Therefore, the CO-valence frequencies are shifted toward shorter wavelengths (**3**, 2050 (m), 1924 (vs) cm^{-1} ; **4**, 2078 (m), 1959 (sh), 1930 (vs) cm^{-1} in CH_2Cl_2). The large downfield shift of the ^{31}P NMR signal from 115.7 to 199.4 ppm is striking, since on protonation the signal is shifted in the opposite direction.^{3,5} On the other hand, one would expect deshielding of the phosphorus when it is directly bound to a quarternary nitrogen with a full positive charge on it. The presence of the NET_2Me group is assured by ^1H NMR spectroscopy. Conductance measurements in acetone are consistent with the formulation of a 1:1 salt.

Compound **4** corresponds to the intermediates which are to be assumed in the fluorination reactions we discussed in eq 1. At present we cannot give a definite explanation for the stability of **4**. However, it is remarkable that the phosphorus in **3** has only one substituent with a lone electron pair, the NET_2 group. So we are of the opinion that at least one nucleophilic group in the neighborhood

of the reacting NET_2 group might be necessary for the activation of the fluorinating properties of the BF_4^- ion.

Experimental Section. All experiments were performed under a nitrogen atmosphere by using Schlenk glassware. The solvents were free from moisture and oxygen.

$(\text{CO})_5\text{CrPF}(\text{NET}_2)_2$. To a 2.20g (5.0 mmol) of **1**, dissolved in 40 mL of CH_2Cl_2 , was added 2.22 g (15.0 mmol) of $[\text{Me}_3\text{O}][\text{BF}_4]$ as the solid. The mixture was heated at reflux for 48 h and then concentrated to 10 mL. Addition of 20 mL of hexane allowed removal of the excess oxonium salt by filtration. After evaporation of the solvent, the product was purified twice by dissolving it in hexane and subsequent by cooling to -78°C ; 1.68 g (87% yield) of a pale yellow oil (**2**) was obtained. Anal. Calcd for $\text{C}_{13}\text{H}_{20}\text{CrFN}_2\text{O}_5\text{P}$ (**2**): C, 40.42; H, 5.22; N, 7.25. Found: C, 40.5; H, 5.2; N, 7.6. IR (hexane): ν_{CO} 2070 (m), 1958 (s), 1944 (vs) cm^{-1} ; δ_{MCO} 674 (m), 659 (m) cm^{-1} ; ν_{PF} 770 (m) cm^{-1} ; δ_{PF} 518 (w) cm^{-1} . MS (70 eV): M^+ 386 (6.2%). $^{19}\text{F}/^{31}\text{P}$ NMR (CD_2Cl_2): δ_{F} -50.05 (d), δ_{P} 198.17 (d), $^1J_{\text{PF}}$ = 1034.5 Hz.

$[(\text{CO})_5\text{CrP}(\text{NET}_2\text{Me})\text{Et}_2][\text{BF}_4]$. Following the procedure given above 1.77 g (5.0 mmol) of **3** was treated with 2.22 g (15.0 mmol) of $[\text{Me}_3\text{O}][\text{BF}_4]$, but instead of hexane, 20 mL ether was added to the concentrated solution to remove excess oxonium salt. The crude product was recrystallized from 1:1 CH_2Cl_2 /hexane to give 1.52 g of **4** as colorless crystals (mp 92°C dec) in 66% yield. Anal. Calcd for $\text{C}_{14}\text{H}_{23}\text{BCrF}_4\text{NO}_5\text{P}$ (**4**): C, 36.94; H, 5.09; N, 3.08. Found: C, 36.7; H, 5.1; N, 3.5. IR (CH_2Cl_2): ν_{CO} 2078 (m), 1959 (sh), 1930 (vs) cm^{-1} . ^{31}P NMR (CD_2Cl_2): δ 199.4. Conductivity in acetone: $\Lambda(\text{C}\rightarrow\text{O}) = 59.6 \pm 0.5 \text{ S}\cdot\text{val}^{-1}\cdot\text{cm}^2$.

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Registry No. **1**, 105502-21-4; **2**, 105502-22-5; **3**, 105502-23-6; **4**, 105502-25-8; $[\text{Me}_3\text{O}][\text{BF}_4]$, 420-37-1; $(\text{CO})_5\text{CrPPh}(\text{NET}_2)_2$, 105502-26-9; $(\text{CO})_5\text{CrP}(-\text{OC}_2\text{H}_4\text{O}-)\text{NET}_2$, 105502-27-0; $(\text{CO})_5\text{CrPPh}(\text{NET}_2)\text{F}$, 105502-28-1; $(\text{CO})_5\text{CrP}(-\text{OC}_2\text{H}_4\text{O}-)\text{F}$, 105502-29-2; $(\text{CO})_5\text{CrPPh}_2\text{NET}_2$, 105502-30-5; $(\text{CO})_5\text{CrPPh}_2\text{F}$, 105502-31-6; *cis*- $(\text{CO})_4\text{Cr}(\text{PPh}_2\text{F})_2$, 105502-32-7; *trans*- $(\text{CO})_4\text{Cr}(\text{PPh}_2\text{F})_2$, 105561-82-8.

Oxametallacyclopentane Derivatives

$(\eta^5\text{-C}_5\text{H}_5)_2\text{MoCH}_2\text{CH}(\text{R}^1)\text{C}(\text{R}^2)(\text{R}^3)\text{O}$ from Substituted Allylic Alcohols and Cationic Molybdenum Trihydride

Takashi Ito* and Tadashi Igarashi

Department of Materials Chemistry, Faculty of Engineering
Yokohama National University, 156 Tokiwadai, Hodogaya-ku
Yokohama 240, Japan

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Summary: The mechanism of formation of a cationic (γ -hydroxyalkyl)molybdenum complex by the reaction of $[(\eta\text{-C}_5\text{H}_5)_2\text{MoH}_3]^+[\rho\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3]^-$ with a substituted allylic alcohol is discussed in terms of the olefin insertion into the Mo-H bond. The former was deprotonated by treatment with NaOH to give the neutral oxametallacycle $(\eta\text{-C}_5\text{H}_5)_2\text{MoCH}_2\text{CH}(\text{R}^1)\text{C}(\text{R}^2)(\text{R}^3)\text{O}$.

Recently we reported the formation of the cationic molybdenum(IV) complexes (**1**), which possess a cyclic γ -hydroxyalkyl structure, by the reaction of cationic tri-