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A Unidentate Thiometalate Complex: (MeCp)(dppe)Ru–S–ReS$_3$

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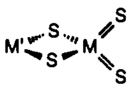
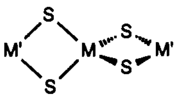
Introduction

Tetrathiometalates, MS_4^{n-} (M = V, Nb, Ta, Mo, W, Re), represent a heavily studied family of inorganic anions.[1] Their use as metallo ligands is of topical interest for the synthesis of heterometallic clusters.[2] Thiometalates coordinate to metals through *pairs* of sulfur atoms; hence they are members of the 1,1-dithiolate class of ligands. Representative bonding modes are shown in A–C.



A



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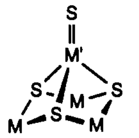

C

In this paper we describe the first example of a monodentate thiometalate complex. This finding is of central importance to thiometalate coordination chemistry because structurally related species are probably involved in the formation of many other thiometalate complexes. This generalization is based on the fact that multidentate ligands usually attach themselves to metals in a stepwise manner, beginning with monodentate coordination.[3]

Our attention was initially drawn to monodentate thiometalates by the isolation of $[CpRu(PPh_3)_2]_2MS_4$ from the reaction of $CpRu(PPh_3)_2OTf$ and MS_4^{2-} at 0 °C (M = Mo, W).[4] Dichloromethane (or toluene) solutions of these tetrakis(phosphine) complexes convert to bis(phosphine) complexes $[CpRu(PPh_3)]_2MS_4$ upon warming to 40 °C (eq 1). We were unable

$$2Cp(PPh_3)_2RuOTf \xrightarrow{MS_4^{2-}} [Cp(PPh_3)_2Ru]_2MS_4 \xrightarrow{-2PPh_3} [Cp(PPh_3)Ru]_2MS_4 \quad (1)$$

to obtain X-ray-quality single crystals of the proposed monodentate thiometalate complexes; however, using ReS_4^-, we have now definitively identified such a species. There exists only one previous example of a heterometallic complex with a single bridging sulfido group.[5]

Results and Discussion

Treatment of a methanolic slurry of (MeCp)Ru(dppe)Cl with 1.0 equiv of solid $(Bu_4N)[ReS_4]$ yields a green precipitate (MeCp = $CH_3C_5H_4$, dppe = $1,2\text{-}(Ph_2P)_2C_2H_4$). The product analyzes as $(MeCp)Ru(dppe)ReS_4$ (**1**; ≈ 89% yield). It is soluble in toluene, THF, and chlorinated hydrocarbons; however, the solutions are not stable for extended periods. The 300-MHz ^1H NMR ($CDCl_3$) spectrum of **1** exhibits the features consistent with the (MeCp)Ru(dppe)X type of molecule, i.e. two MeC_5H_4 multiplets and two PCH_2CH_2P multiplets. We observe a single ^{31}P NMR resonance at 85.6 ppm downfield of external 85% H_3PO_4 (vs 80.9 ppm for (MeCp)Ru(dppe)Cl).

The structure of **1** consists of a tetrahedral ReS_4 subunit with S–Re–S angles ranging from 106.5 (1) to 110.5 (1)°. The Re–S_t distances are relatively short (2.115 (3)–2.130 (3) Å) and are similar to the Re–S distances in $(BuN_4)[ReS_4]$, which range from 2.118 (3) to 2.126 (6) Å.[6] The Re–S_b distance is longer, with a length of 2.171 (3) Å; this value compares well with those in $[Cl_2Fe(ReS_4)FeCl_2]^{2+}$ (2.187 (3)–2.208 (3) Å), as reported for the mixed-crystal compound $(PPh_4)_2[Cl_2Fe(ReS_4)FeCl_2]_{0.7}[Cl_2Fe(MoS_4)FeCl_2]_{0.3}$.[7] The Ru–S distance in **1** is 2.339 (3) Å, while, by comparison, $[CpRu(MeNC)]_2WS_4$ has Ru–S_b distances of 2.394 (6) and 2.377 (6) Å.[8] Shorter Ru–S bonds in ruthenium sulfides are found in compounds where Ru–S π-bonding is indicated, e.g. $(C_5Me_5)_2Ru_2S_4$ and $[CpRu(PR_3)_2]_2(\mu\text{-}S_2)^{2+}$.[9]

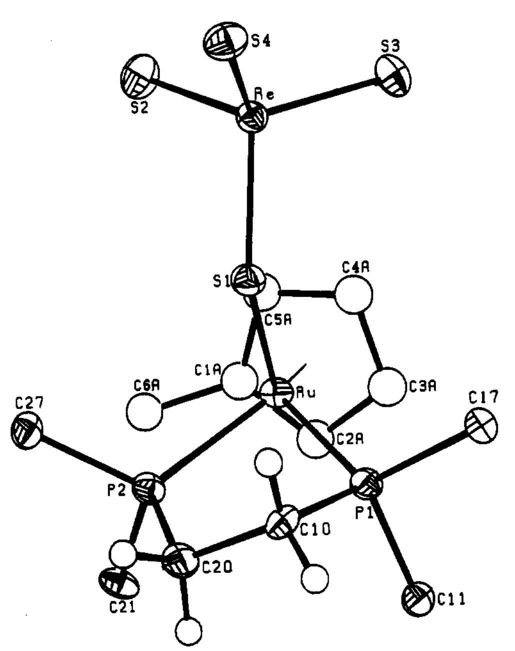

Figure 1. Structure of $(MeCp)(dppe)RuSReS_3$ with thermal ellipsoids drawn at the 35% probability level. Only the ipso carbon atoms of the phenyl rings are shown.

The infrared spectrum of **1** (KBr) shows a ν_{Re-S} band at 490 cm^{-1}, which is similar in energy to that for $(Bu_4N)[ReS_4]$ (KBr, 484 cm^{-1}). In contrast, ν_{Re-S} is 451 cm^{-1} for the salt $[PPh_4]_2[NEt_4][Cl_7Cu_5(\mu\text{-}ReS_4)]$, where ReS_4 is bidentate.[10]

Previous work has shown that WS_4^{2-} and MoS_4^{2-} are acceptor ligands insofar as their complexes are more difficult to oxidize than the corresponding chlorides. A striking manifestation of the acceptor properties of the tetrathiometalates is the stability of the cobalt(I) and iron(I) complexes $M(WS_4)_2^{3-}$.[11] In the case of **1**, the ReS_4^- ligand is a sufficiently strong acceptor ligand to permit reduction, unprecedented for a $CpRuL_2X$ complex. In THF (Pt electrode) one-electron reduction occurs at $E_{1/2}$ = −800 mV vs Ag/AgCl; the $|E_{p,c} - E_{p,a}|$ value of 90 mV is similar to that of ferrocene under the same conditions. The linear dependence of i_p on the square of the scan rate indicates that the rate of reduction is under diffusion control. The value of $i_{p,c}/i_{p,a}$ is 0.7, indicative of a quasi-reversible process and suggesting that the monoanion decomposes on the time scale of the cyclic voltammetry experiment. In contrast, the substitution and redox properties of the compounds $(RCp)Ru(PR_3)_2SR$ (R = H, alkyl) indicate that they

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[1] M = V, Mo, W, Re: Müller, A.; Diemann, E.; Jostes, R.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934; *Angew. Chem.* **1981**, *93*, 957. M = Nb, Ta: Lee, S. C.; Holm, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 9654.

[2] Howard, K. E.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1988**, *27*, 3561. Howard, K. E.; Lockemeyer, J. R.; Massa, M. A.; Rauchfuss, T. B.; Wilson, S. R.; Yang, X. *Inorg. Chem.* **1990**, *29*, 4385 and references therein.

[3] Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*; Wiley: New York, 1967; p 223.

[4] Howard, K. E. Ph.D. Dissertation, University of Illinois at Urbana-Champaign, 1988.

[5] Bergman, R. G.; Kovacs, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 1131.

[6] Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 4635.

[7] Müller, A.; Jostes, R.; Schmitz, K.; Krickemeyer, E.; Bögge, H.; Bill, E.; Trautwein, A. *Inorg. Chim. Acta* **1988**, *149*, 9.

[8] Howard, K. E.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1988**, *27*, 1710.

[9] Amarasekera, J.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1987**, *26*, 3328. Rauchfuss, T. B.; Rodgers, D. P. S.; Wilson, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 3114.

[10] Müller, A.; Krickemeyer, E.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 990; *Angew. Chem.* **1986**, *98*, 987.

[11] (a) M = Fe: Stremple, P.; Baenziger, N. C.; Coucouvanis, D. *J. Am. Chem. Soc.* **1981**, *103*, 4601. (b) M = Co: Müller, A.; Hellman, W.; Schneider, J.; Schimanski, U.; Demmer, U.; Trautwein, A.; Bender, U. *Inorg. Chim. Acta* **1982**, *65*, L41.

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Table I. Crystallographic Data for (MeCp)(dppe)RuSReS$_3$·Et$_2$O

chem formula	$C_{32}H_{31}P_2ReRuS_4 \cdot C_4H_{10}O$
a	12.984 (4) Å
b	19.312 (8) Å
c	16.296 (6) Å
α	90°
β	106.27 (3)°
γ	90°
V	3922 (5) Å^3
Z	4
fw	893.06 + 74.12
space group (No.)	$P2_1/n$ (14)
T	–75 °C
λ(Mo Kα)	0.71073 Å
ρ_{calcd}	1.638 g/cm^3
μ	38.15 cm^{-1}
$R(F_o)^a$	0.050
$R_w(F_o)^a$	0.063

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, where $w = k/[(\sigma(F_o))^2 + (pF_o)^2]$.

are quite electron rich.[12] In fact, even WS$_4$-bridged compounds [(RCp)RuL]$_2$(μ-WS$_4$) where L = RNC, R$_3$P, and CO are susceptible to oxidation at mild potentials.[8] Collectively our observations suggest that monodentate ReS$_4^-$ is a very strong acceptor ligand.

Preliminary studies show that **1** reacts (25 °C) with H$_2$ (1 atm) and ethylene, as well as a variety of alkenes and alkynes. Since the ruthenium center is electronically saturated, the primary site of reactivity is likely to be the thiometalate. Detailed studies however have been limited by the instability of the products.

To summarize, we have succeeded in characterizing the first example of a monodentate thiometalate complex. Our approach capitalized on the low basicity of ReS$_4^-$ and the availability of only one coordination site on the (RCp)Ru(PR$_3$)$_2^+$ electrophile. Additional stabilization of the η^1-ReS$_4$ ligand may derive from the strong π-donor properties of the Ru(II) center. Our results suggest that the electrophilic reactivity of monodentate thiometalates is enhanced relative to that of their bidentate derivatives.

Experimental Section

All reactions were carried out under a nitrogen atmosphere. Methanol was dried over molecular seives. Diethyl ether was distilled from benzophenone ketyl. (MeCp)Ru(dppe)Cl was prepared analogously to the literature preparation of CpRu(dppe)Cl.[13] [Et$_4$N]ReS$_4$ was prepared according to literature methods.[6]

^{1}H NMR spectra were recorded on a General Electric QE-300 spectrometer using CDCl$_3$ as the solvent; the data are reported in ppm versus TMS. ^{31}P{^{1}H} NMR spectra were recorded on a General Electric GN-300 spectrometer operating at 121.46 MHz. Infrared spectra were obtained on a Perkin-Elmer 1750 FT-IR spectrophotometer. Elemental analyses were performed by the University of Illinois Microanalytical Laboratory.

(MeCp)Ru(dppe)ReS$_4$ (1). To a slurry of 330.8 mg of (MeCp)Ru(dppe)Cl (0.539 mmol) in 60 mL of methanol was added 300.0 mg of solid [Et$_4$N]ReS$_4$ (0.539 mmol) and the mixture stirred for 18 h. The resulting dark green solid was isolated via filtration, washed with methanol and ether, and dried in vacuo to give 427.2 mg of **1** (0.478 mmol) as a dark green solid (89% yield). Anal. Calcd for $C_{32}H_{31}P_2ReRuS_4$: C, 43.04; H, 3.50; P, 6.94. Found: C, 43.38; H, 3.85; P, 6.59. ^{1}H NMR (CDCl$_3$): δ 1.29 (s), 2.6 (m), 4.58 (s), 4.90 (s), 7.2 (br m). ^{31}P NMR (vs 85% H$_3$PO$_4$, CDCl$_3$): δ 85.9. IR (KBr): $\nu_{\text{Re-S}}$ = 490 cm^{-1}.

Table II. Selected Positional Parameters for (MeCp)(dppe)RuSReS$_3$·Et$_2$O^a

	x/a	y/b	z/c
Re	0.05684 (4)	0.23562 (3)	0.49591 (4)
Ru	–0.23425 (8)	0.15736 (6)	0.37984 (7)
S1	–0.0657 (3)	0.1563 (2)	0.4806 (2)
S2	0.0003 (3)	0.3310 (2)	0.5326 (3)
S3	0.0966 (3)	0.2485 (2)	0.3787 (3)
S4	0.1916 (3)	0.2002 (2)	0.5928 (3)
P1	–0.2042 (3)	0.0419 (2)	0.3644 (2)
P2	–0.3095 (3)	0.1172 (2)	0.4821 (2)
C1A	–0.3489 (9)	0.2504 (7)	0.3239 (8)
C2A	–0.3650	0.1932	0.2669
C3A	0.2672	0.1803	0.2468
C4A	–0.1905	0.2295	0.2915
C5A	–0.2410	0.2728	0.3392
C6A	–0.4206	0.2697	0.3790
C10	–0.1854 (9)	–0.0003 (7)	0.4677 (8)
C11	–0.3090 (9)	–0.0071 (7)	0.2922 (9)
C17	–0.0887 (9)	0.0164 (7)	0.3281 (8)
C20	–0.2743 (9)	0.0256 (7)	0.5068 (9)
C21	–0.4560 (9)	0.1161 (7)	0.4495 (9)
C24	–0.679 (1)	0.1215 (8)	0.387 (1)
C27	–0.2761 (9)	0.1599 (7)	0.5868 (9)

[a] Disordered cyclopentadienyl ring was "idealized" and converged with a relative occupancy factor of 0.537 (2) for position A; disordered diethyl ether molecules were "idealized" and converged with relative occupancy factors 0.295 (7), 0.216 (8), 0.249 (7), and 0.240 (7) for positions A–D, respectively.

Table III. Selected Bond Distances (Å) and Angles (deg) for (MeCp)(dppe)RuSReS$_3$·Et$_2$O

Re–S1	2.173 (4)	Ru–P1	2.290 (4)
Re–S2	2.130 (4)	Ru–P2	2.290 (4)
Re–S3	2.129 (4)	C–C(Cp ring)	1.42 (2)
Re–S4	2.115 (4)	Ru–CpA^a	1.89 (1)
Ru–S1	2.339 (3)		

S1–Re–S3	109.5 (1)	S1–Ru–P1	85.1 (1)
S1–Re–S2	110.1 (1)	S1–Ru–P2	89.6 (1)
S1–Re–S4	106.5 (1)	S2–Re–S3	109.9 (2)
S1–Ru–CpA^a	125.2 (4)	Re–S1–Ru	125.8 (2)

[a] CpA (CpB) is the centroid of one rotamer of the disordered A (B) Cp ring.

X-ray Structure Determination. Dark, opaque crystals of the diethyl ether solvate of **1** suitable for X-ray crystallography were obtained by layering a CHCl$_3$ solution of (MeCp)Ru(dppe)ReS$_4$ with diethyl ether. A crystal with the approximate dimensions of 0.2 × 0.2 × 0.3 mm was mounted with oil (Paratone-N, Exxon) to a thin glass fiber and then cooled to –75 °C with the (0,–3,–1) scattering plane roughly normal to the spindle axis. Data were collected with a Enraf-Nonius CAD4 automated κ-axis diffractometer. Standard peak search and automatic procedures, followed by least-squares refinement using 25 reflections (17.6° ≤ 2θ ≤ 26.7°), yielded the cell dimensions given in Table I. A total of 6136 unique reflections (R_i = 0.016) in the range 2.0° < 2θ < 32.0°, among which were 4479 observed reflections ($I > 2.58\sigma(I)$), were collected by scanning $\pm h,-k,-l$ at a variable scan rate over 58.10 h, with no change in the appearance in the crystal. Lorentz, polarization, and anomalous dispersion corrections were applied, the absorption numerical correction was applied with maximum and minimum transmission factors of 0.588 and 0.364, respectively.

The structure was solved by Patterson methods (SHELXS-86); the correct rhenium and ruthenium positions were deduced from a vector map, and partial structure expansion gave positions of the sulfur, phosphorus, and five carbon atoms. Subsequent least squares-difference Fourier calculations revealed positions for the remaining non-hydrogen atoms and disordered diethyl ether solvent molecules. Ordered hydrogen atoms were included as fixed contributors in "idealized" positions. Hydrogen atoms on the disordered cyclopentadienyl ligand and solvent molecules were not included in structure factor calculations. The MeCp ring in the crystal is disordered between two positions due to different orientations of the methyl group. In the final cycle of least squares, common isotropic thermal parameters were varied for the disordered diethyl ether, cyclopentadienyl, and hydrogen atoms; anisotropic thermal coefficients were refined for the remaining non-hydrogen atoms. Disordered diethyl ether bond lengths and angles were constrained. Successful convergence was indicated by the maximum shift/error for the final cycle. The highest peaks in the final difference Fourier map were in the vicinity of the disordered solvent molecules; the proposed model does not ideally account for all of the multiply disordered solvent molecule positions. A final analysis of variance between observed and calculated structure factors showed an inverse dependence on sin θ.

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(12) Amarasekera, J.; Rauchfuss, T. B. *Inorg. Chem.* **1989**, *28*, 3875. Shaver, A.; Plouffe, P. Y.; Livingstone, E. *Inorg. Chem.* **1990**, *29*, 1826. Treichel, P. M.; Schmidt, M. S.; Crane, R. A. *Inorg. Chem.* **1991**, *30*, 379.

(13) Ashby, G. S.; Bruce, M. I.; Tomkins, I. B.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1003.

Johnson Matthey. We are grateful to Dr. Kevin Howard for preliminary studies.

Registry No. **1**, 136316-89-7; (MeCp)Ru(dppe)Cl, 118211-56-6; $\mathrm{[Et_4N]ReS_4}$, 103517-31-3.

Supplementary Material Available: Tables of bond distances and angles, atomic coordinates, and thermal parameters (3 pages); a listing of structure factors (30 pages). Ordering information is given on any current masthead page.

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Disproportionation of the Bis(benzene)chromium Cation Induced by Pyridine. Crystal and Molecular Structure of Two Tetrapyridine Complexes Containing Chromium(II) and Chromium(III)[1]

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Disporportionation of bis(arene)chromium(I) cations has been known since many years, though the reports have been sparse and sometimes contradictory.[2,3]

Among the bases which promote that reaction, 2,2′-bipyridyl appeared to be particularly indicated,[2c] especially because of its chelating properties, which can stabilize Cr(II) and Cr(III) in the form of hexacoordinated complexes. Usually, this is not the case for the related monodentate base pyridine, which seldom yields stable homoleptic structurally established hexacoordinated complexes.[4] In fact, though $\mathrm{Mo(arene)_2}^+$ cations readily undergo hydrolytic disproportionation in the presence of aqueous hydroxides,[2a] their oxidation state does not change on moderate heating in neat pyridine.[5]

Nevertheless, the importance of pyridine in the rich and recently clarified disproportionation chemistry of metal carbonyls, another class of low-valent transition-metal complexes,[6] has prompted us to investigate its effects on the $\mathrm{Cr(C_6H_6)_2}^+$ cation. We report here that the bis(η^6-benzene)chromium cation disproportionates in pyridine.

Experimental Section

Chemicals. All operations were carried out under an inert atmosphere. Bis(η^6-benzene)chromium hexafluorophosphate was synthesized in 82% yield from bis(η^6-benzene)chromium[2b] by the same procedure as for the corresponding iodide.[2b] Reagent grade pyridine was refluxed 24 h over $\mathrm{CaH_2}$ prior to distillation. Reagent grade toluene was refluxed 3 h over Na and then distilled.

Analyses. Elemental analyses were carried out under an inert atmosphere by Microanalytisches Labor Pascher, Remagen, Germany.

Disproportionation Reaction. A 0.18 M solution of bis(η^6-benzene)chromium hexafluorophosphate in pyridine was kept at 75 °C during 8 h. Violet crystals of $\mathrm{[Cr(py)_4(PF_6)_2]\cdot 2py}$ (**1**) (py = pyridine) separated out in 23% yield and were washed with pyridine, which was collected together with the mother liquor. After concentration in vacuo to five-sixths of the initial volume, the clear solution was cooled overnight to −26 °C. This caused black crystals of bis(η^6-benzene)chromium to precipitate (22%). The mother liquor was then diluted 1:1 with toluene and then filtered. The resulting clear solution was kept overnight at −26 °C, yielding pink leaflets of $\mathrm{Cr(py)_5F_2(PF_6)}$ (**2**) (10%). Satisfactory complete elemental analyses were obtained for all the reported products ($\mathrm{CrC_{30}H_{30}N_6P_2F_{12}}$ (**1**); $\mathrm{CrC_{25}H_{25}N_5PF_8}$ (**2**)). To grow a single crystal, **2** was recrystallized from hot ethanol, yielding *trans*-$\mathrm{[Cr(py)_4F_2]PF_6}$ (**3**).

Table I. Crystallographic Data for **1** and **3**

	1
$\mathrm{C_{30}H_{30}N_6CrF_{12}P_2}$	fw = 816.5
a = 11.375 (1) Å	space group $I422$ (No. 97)
c = 14.084 (1) Å	ρ_{calc} = 1.488 g cm^{-3}
V = 1822.1 Å^3	μ = 4.812 cm^{-1}
Z = 2	$R(F_o)$ = 0.049
T = 18 °C	$R_w(F_o)$ = 0.045
λ = 7.1069 Å	
	3
$\mathrm{C_{20}H_{20}N_4CrF_8P}$	fw = 551.4
a = 12.210 (6) Å	space group $C2/c$ (No. 15)
b = 14.177 (3) Å	λ = 1.5418 Å
c = 13.994 (5) Å	ρ_{calc} = 1.591 g cm^{-3}
β = 107.55 (3)°	μ = 55.861 cm^{-1}
V = 2301.5 Å^3	$R(F_o)$ = 0.064
Z = 4	$R_w(F_o)$ = 0.065
T = 18 °C	

Table II. Selected Bond Lengths (Å) and Angles (deg) for **1** and **3**

Bond Lengths for **1**			
Cr–N1	2.113 (3)	P–F3	1.566 (6)
Cr···F1	2.449 (5)	N1–C1	1.329 (5)
P–F1	1.613 (6)	C1–C2	1.375 (9)
P–F2	1.565 (3)	C2–C3	1.356 (7)
Bond Angles for **1**			
F1···Cr···F1′	180.0	C2–C3–C2′	116.7 (7)
N1–Cr–N1′	180.0	F1–P–F2	88.8 (2)
N1–Cr–N1″	90.0	F1–P–F3	180.0
Cr–N1–C1	121.2 (2)	F2–P–F2′	177.6 (3)
C1–N1–C1′	117.7 (5)	F2–P–F2″	90.0 (3)
N1–C1–C2	121.8 (5)	F2–P–F3	91.2 (2)
C1–C2–C3	121.0 (6)		
Bond Lengths for **3**			
Cr–F1	1.853 (2)	P–F21	1.490 (7)
Cr–N1	2.085 (2)	P–F22	1.508 (4)
Cr–N2	2.095 (2)	P–F23	1.560 (3)
N1–C11	1.328 (4)	P–F24	1.477 (7)
N1–C15	1.345 (4)	F1′···H11	2.395 (2)
N2–C21	1.325 (5)	F1···H15	2.389 (2)
N2–C25	1.338 (4)	F1′···H21	2.324 (2)
C–C	1.352 (5)–1.393 (5)	F1···H25	2.395 (2)
Bond Angles for **3**			
F1–Cr–F1′	179.2 (1)	Cr–N1–C11	121.9 (2)
F1–Cr–N1	89.88 (9)	Cr–N1–C15	120.5 (3)
F1–Cr–N1′	89.58 (9)	C11–N1–C15	117.5 (3)
F1–Cr–N2	91.0 (1)	Cr–N2–C21	120.5 (2)
F1–Cr–N2′	89.6 (1)	Cr–N2–C25	120.7 (2)
N1–Cr–N1′	91.9 (1)	C21–N2–C25	118.6 (3)
N1–Cr–N2	91.34 (9)	F21–P–F22	89.4 (3)
N1–Cr–N2′	176.7 (2)	F21–P–F23	90.2 (2)
N2–Cr–N2′	85.4 (1)	F21–P–F24	180.0

X-ray Data Collection. A crystal of **1** with the approximate dimensions (mm) 0.4 × 0.35 × 0.35 was mounted under $\mathrm{N_2}$ in a glass capillary for intensity data collection. The structure was solved using direct methods.[7] Refinement of the $\mathrm{[Cr(py)_4]^{2+}}$ ion and the $\mathrm{PF_6}^-$ counterion

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(2) (a) Fischer, E. O.; Fritz, H. P. *Adv. Inorg. Chem. Radiochem.* **1959**, *1*, 55. (b) Fischer, E. O. *Inorg. Synth.* **1960**, *6*, 132. (c) Hein, F.; Scheel, H. *Z. Anorg. Allg. Chem.* **1961**, *312*, 264.

(3) Davis, R.; Kane-Maguire, L. A. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, England, 1982; Vol. 3, p 977.

(4) (a) Doedens, R. J.; Dahl, L. F. *J. Am. Chem. Soc.* **1966**, *88*, 4847. (b) Templeton, J. L. *Ibid.* **1979**, *101*, 4906.

(5) Silverthorn, W. E. *Inorg. Chem.* **1979**, *18*, 1835. A study aimed at clarifying the chemical behavior at higher temperatures is in progress (G. Fochi).

(6) Mealli, C.; Proserpio, D. M.; Fachinetti, G.; Funaioli, T.; Fochi, G.; Zanazzi, P. F. *Inorg. Chem.* **1989**, *28*, 1122 and references therein.

(7) Sheldrick, G. M. SHELXS-86. University of Göttingen, Göttingen, FRG, 1986.

0020-1669/91/1330-4669$02.50/0