

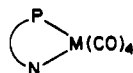
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4,5-Dimethyl-2-(2-pyridyl)phosphorin as a Chelating Ligand. Synthesis and X-ray Crystal Structure Analysis of (4,5-Dimethyl-2-(2-pyridyl)phosphorin)tetracarbonylchromium

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4,5-Dimethyl-2-(2-pyridyl)phosphorin, the first known phosphorus analogue of 2,2'-bipyridine, reacts through its nitrogen atom with anhydrous HCl to give a stable monohydrochloride. With Cr(CO)₅(THF) and W(CO)₅(THF), it gives first a P-M(CO)₅ complex, which readily cyclizes with loss of CO to give the corresponding chelates



(M = Cr, W). The same type of chelate is obtained by reaction with Mo(CO)₆ in a sealed tube at 155 °C. We have performed the X-ray structure analysis of the chromium chelate. Crystal data for C₁₆H₁₂CrNO₄P are $a = 12.955$ (5) Å, $b = 18.943$ (8) Å, $c = 6.635$ (3) Å, $\beta = 91.83$ (2)°, $V = 1627$ Å³, $Z = 4$, d_{calc} = 1.491 g cm⁻³, and space group $P2_1/n$. No cooperativity is observed between the phosphorin and pyridine rings: the N-Cr-CO (trans) unit has strictly the same bond lengths as in (py)Cr(CO)₅, and the C-C bridge between the phosphorin and pyridine units has the same length as the bridge in free 2,2'-bipyridine, 1.490 (6) Å. The phosphorin unit appears to be a far better ligand than 2,4,6-triphenylphosphorin in its P-Cr(CO)₅ complex: P-Cr = 2.280 (1) Å in the chelate vs. 2.372 (4) Å in the phosphorin Cr(CO)₅ complex. The intracyclic P=C bond lengths are especially short: 1.708 (4) vs. ca. 1.73-1.74 Å in free phosphorins.

Introduction

2,2'-Bipyridyls are among the most widely used ligands in coordination chemistry. They coordinate efficiently to either "hard" or "soft" metals and stabilize high and low oxidation states as well. Their metal complexes have interesting photochemical, redox, and catalytic behaviors, which have been described in several reviews.^{2,3} A renewed interest in that field has recently arisen with the discovery of the possible uses of Ru(bpy)₃²⁺ for the photocatalytic splitting of water.⁴ Broadly speaking, the high efficiency of bipyridyls as ligands stems from both their chelating ability and a balance between their σ -donor and π -acceptor properties, which can be adjusted to the electronic requirements of the complexed metals.

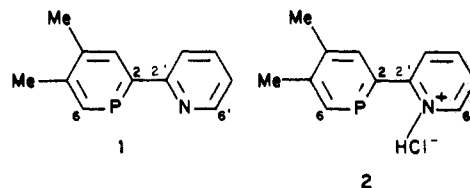
On another side, 2-phosphino- and 2-phosphinomethyl-substituted pyridines have recently found an increasing use as chelating or bridging phosphorus-nitrogen ligands.⁵ A part of their interest as ligands lies in the presence of the relatively labile N donor end suggesting possible uses in catalysis.

With such a background, the discovery in our laboratory of the first known phosphorus analogue of 2,2'-bipyridyls, i.e. 4,5-dimethyl-2-(2-pyridyl)phosphorin (**1**),⁶ was particularly exciting. We launched immediately a program for evaluating the potential of this ligand in coordination chemistry. The first

results of that work are described hereafter.

Results and Discussion

Whereas pyridine has a sizable basicity ($\text{p}K_{\text{a}} = 5.25$ in water⁷), phosphorin has no measurable $\text{p}K_{\text{a}}$. Indeed, calculations suggest a value close to -10 for the parent ring.⁸ Thus, we expected that the 2-(2-pyridyl)phosphorin **1** would be monobasic.

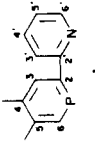
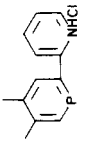
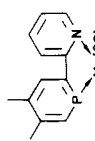
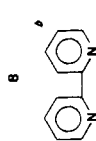


We have not measured precisely the $\text{p}K_{\text{a}}$ of **1**, which is probably close to that of 2,2'-bipyridine (i.e. 4.33 in water according to a critical review of the literature data⁹), but we have checked that it is possible to obtain the stable monohydrochloride **2** by just reacting anhydrous HCl with **1** in ether. The protonation takes place at nitrogen since the largest H...P coupling in **2** involves H-C₆ ($^2J(\text{H-P}) \approx 41$ Hz) excluding the formation of a P-H bond. The comparison between the ¹³C NMR data of **1** and **2** is particularly interesting (see Table I). The protonation of nitrogen leads to a shielding of the C₂ and C₆ carbons by 4.7 and 4.3 ppm, respectively. That the phenomenon has approximately the same magnitude on both sides of the pyridine ring suggests that the phosphorin plays no role in it. The situation is entirely different in the phosphorin ring. Whereas C₆ is practically unaffected, C₂ is shielded by 12.7 ppm while phosphorus is deshielded by 11.7 ppm. Thus, when the electron-attracting character of the

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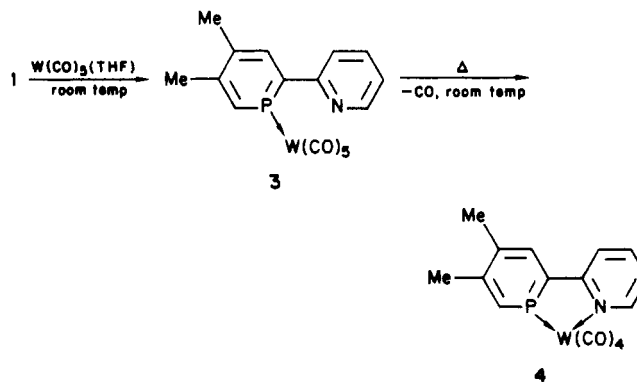
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Table I. ^{13}C NMR Data^a

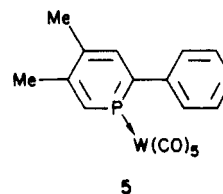
	C_2	C_3	C_4	C_5	C_6	C_2'	C_3'	C_4'	C_5'	C_6'	Me_4	Me_5
	165.86 (45.9)	135.89 (13.7)	139.67 (17.6)	143.42 (14.7)	154.55 (43.8)	159.61 (24.4)	120.94 (14.7)	136.76 (0)	122.22 (2)	149.65 (0)	22.47 (2)	23.06 (3.9)
	153.19 (48.8)	138.41 (13.7)	141.46 (15.7)	146.87 (14.7)	154.45 (48.8)	154.77 (26.6)	125.23 (19.5)	141.61 (0)	124.26 (0)	145.39 (0)	21.99 (0)	23.06 (3.9)
	159.69 (17.1)	134.31 (12.2)	135.58 (22.0)	148.79 (17.1)	145.88 (7.3)	154.91 (9.8)	118.98 (12.2)	137.52 (0)	122.77 (3.7)	156.15 (3.7)	22.62 (3.7)	23.95 (8.5)
						155.5	125.8	138.02	122.73	153.68		

^a All values shown are in δ with $J_{\text{P-C}}$ values in parentheses (in Hz); the solvent used was CDCl_3 + internal Me_4Si . ^b Reference 11.

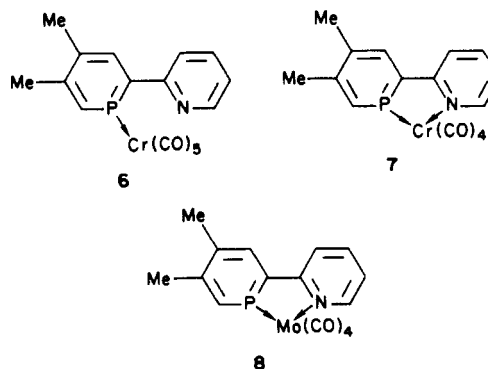
pyridine substituent is increased, a huge accumulation of negative charge occurs on the substituted α -carbon of the phosphorin ring due to a strong polarization of the corresponding $\text{P}=\text{C}$ double bond. These two observations support the idea that there is no possible π -electron flow from the phosphorin to the pyridine ring. The consequences of the protonation at nitrogen are indeed better explained if the interaction between both rings is purely inductive. This means that the bridging bond $\text{C}_2\text{-C}_2'$ is a pure σ single bond with no π character. According to these preliminary experiments, we thought that 2-(2-pyridyl)phosphorin behaved as a superposition of two independent units, the soft phosphorin and the hard pyridine ligands. Thus, we expected that the coordination of **1** to low-valent soft metals would take place in two separate steps including a preliminary complexation at phosphorus followed by a ring closure through coordination of nitrogen. We checked this hypothesis by studying the reaction of **1** with $\text{W}(\text{CO})_5(\text{THF})$. The mono complex **3** is first obtained. This



complex was characterized by IR and ^{31}P NMR spectroscopy. The ^{31}P NMR data for **3** are very close to those of the independently made complex **5**: $\delta_{31\text{P}}(\text{5}) = 151.7$ (CDCl_3), $^1J(^{31}\text{P}\text{-}^{183}\text{W}) = 261.5$ Hz, ^{31}P coordination chemical shift -29.8 ppm; $\delta_{31\text{P}}(\text{3}) = 160.5$, $^1J(^{31}\text{P}\text{-}^{183}\text{W}) = 273$ Hz, ^{31}P coordination chemical shift -24.4 ppm.



In fact, this complex **3** is unstable and cannot be isolated in the pure state. It spontaneously loses carbon monoxide to give the chelate **4**. The ring closure is accompanied by a strong downfield shift of the ^{31}P resonance: $\delta_{31\text{P}}(\text{4}) = 205.2$, $^1J(^{31}\text{P}\text{-}^{183}\text{W}) = 271$ Hz. The same general picture is observed when $\text{W}(\text{CO})_5(\text{THF})$ is replaced by $\text{Cr}(\text{CO})_5(\text{THF})$. We first obtained the η^1 $\text{P-Cr}(\text{CO})_5$ complex **6** ($\delta_{31\text{P}} = 208.6$ in C_6D_6),



which spontaneously cyclized to give the chelate **7** ($\delta_{31\text{P}} = 247.7$)

Table II. Positional Parameters and Their Estimated Standard Deviations^a

atom	x	y	z	B, Å ²
Cr	0.24339 (9)	0.02734 (5)	0.0560 (2)	2.92 (2)
P	0.1710 (1)	0.11538 (8)	-0.1355 (3)	3.04 (3)
C1	0.0990 (5)	0.1354 (4)	-0.348 (1)	3.4 (1)
C2	0.0746 (5)	0.2038 (3)	-0.405 (1)	3.2 (1)
C3	0.1085 (5)	0.2639 (3)	-0.297 (1)	3.4 (1)
C4	0.1676 (5)	0.2585 (3)	-0.118 (1)	3.3 (1)
C5	0.2005 (5)	0.1957 (3)	-0.031 (1)	2.7 (1)
C6	0.2637 (5)	0.1904 (3)	0.160 (1)	3.0 (1)
C7	0.2959 (6)	0.2490 (4)	0.269 (1)	3.9 (2)
C8	0.3541 (6)	0.2405 (4)	0.444 (1)	4.5 (2)
C9	0.3795 (6)	0.1740 (4)	0.505 (1)	4.4 (2)
C10	0.3459 (6)	0.1178 (4)	0.395 (1)	3.7 (1)
N	0.2893 (4)	0.1234 (3)	0.2201 (8)	3.1 (1)
C11	0.0107 (6)	0.2131 (4)	-0.599 (1)	4.6 (2)
C12	0.0782 (7)	0.3362 (4)	-0.369 (1)	4.8 (2)
C13	0.3673 (6)	0.0284 (3)	-0.097 (1)	3.6 (1)
C15	0.3036 (6)	-0.0354 (3)	0.237 (1)	3.9 (2)
O1	0.4380 (5)	0.0251 (3)	-0.1927 (8)	5.6 (1)
O3	0.3390 (5)	-0.0775 (3)	0.3463 (8)	6.1 (1)
O4	0.0441 (5)	0.0051 (4)	0.275 (1)	7.4 (2)
C14	0.1993 (6)	-0.0451 (4)	-0.106 (1)	4.2 (2)
C16	0.1206 (6)	0.0161 (4)	0.199 (1)	4.4 (2)
O2	0.1725 (5)	-0.0922 (3)	-0.2058 (9)	6.8 (1)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{1}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos \gamma)B_{12} + ac(\cos \beta)B_{13} + bc(\cos \alpha)B_{23}]$.

in C₆D₆). The Mo(CO)₄ chelate **8** was obtained through an entirely different approach by directly reacting Mo(CO)₆ with **1** at 155 °C in a sealed tube. Of course, the P→Mo(CO)₅ η₁ complex was not formed in a notable amount in that case.

The ¹³C NMR spectrum of **8** (Table I) has been interpreted with the help of the corresponding data for complex **5**, for the unsubstituted phosphorin-*P* complexes,¹⁰ and for (bpy)Mo(CO)₄.¹¹ The observed trends upon complexation are similar for the whole series. For example, we note a substantial decrease of ¹J(P-C) couplings upon complexation when comparing the ¹³C data of complexes **5** and **8** with those of the corresponding free ligands. Unfortunately, these observations give no clue for the electronic structure of **8**. Thus, in order to get more precise information on that point and also on the geometrical structure of the ligand, we performed an X-ray crystal structure analysis of the chromium chelate complex **7**.

Table II gives the atomic positional parameters for all atoms of **7**. Table III gives selected bond lengths and angles with their estimated standard deviations. Table V (supplementary material) gives the least-squares planes of interest.

In the crystalline state, **7** consists of discrete molecules only linked by hydrogen bonds and van der Waals interactions with no unusual intermolecular contacts.

Figure 1 shows a molecule of **7** with the labeling scheme used. The coordination polyhedron of the chromium atom is a deformed octahedron, four corners of which are occupied by carbonyl groups and the remaining two by the heteroatoms of the phosphorin-pyridine ligand. The ligand is planar within experimental error as seen from Table V; PL1 is a pseudo mirror plane for the Cr(CO)₄ moiety.

In complexes of 2,2'-bipyridine with low-valent metals, it has been theoretically predicted¹² and experimentally demonstrated¹³ that the electron population of the LUMO of the ligand (π back-bonding) leads to a shortening of the C-C

Table III. Selected Bond Lengths (Å) and Angles (deg) with Their Estimated Standard Deviations

Cr-P	2.280 (1)	C4-C5	1.384 (6)
Cr-N	2.193 (4)	C5-C6	1.490 (6)
Cr-C13	1.928 (7)	C6-C7	1.383 (6)
Cr-C14	1.825 (5)	C7-C8	1.375 (7)
Cr-C15	1.843 (5)	C8-C9	1.360 (7)
Cr-C16	1.889 (7)	C9-C10	1.354 (7)
P-C1	1.707 (5)	C2-C11	1.513 (7)
P-C5	1.709 (4)	C3-C12	1.499 (7)
N-C6	1.367 (5)	C13-O1	1.132 (7)
N-C10	1.358 (6)	C14-O2	1.156 (6)
C1-C2	1.385 (6)	C15-O3	1.164 (6)
C2-C3	1.411 (7)	C16-O4	1.145 (7)
C3-C4	1.393 (7)		
Cr-P-C3	162.1 (2)	N-Cr-C14	172.7 (2)
Cr-N-C8	176.6 (3)	N-Cr-C15	96.3 (2)
P-Cr-N	76.7 (1)	N-Cr-C13	92.1 (2)
C6-N-Cr	124.4 (3)	N-Cr-C16	93.6 (2)
C10-N-Cr	119.3 (3)	C1-P-C5	104.2 (2)
C1-P-Cr	145.7 (2)	C6-N-C10	116.2 (4)
C5-P-Cr	110.0 (2)	N-C6-C5	115.6 (3)
P-Cr-C15	172.7 (2)	P-C5-C6	113.2 (3)
P-Cr-C14	96.1 (2)	N-C10-C9	123.6 (4)
P-Cr-C16	91.3 (2)	P-C1-C2	123.4 (4)
P-Cr-C13	91.9 (2)	P-C5-C4	122.2 (3)

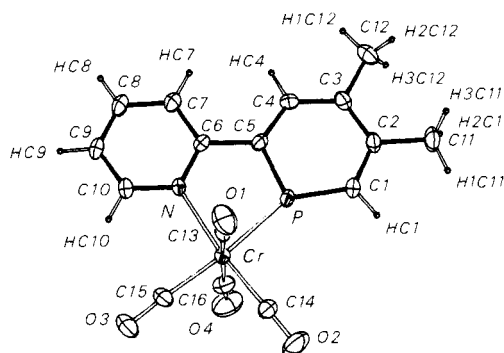


Figure 1. ORTEP plot of one molecule of **7**. Ellipsoids are scaled to enclose 40% of the electronic density. Hydrogen atoms have arbitrary radii.

bridge between the two pyridine units and to a lengthening of the N-C(bridge) bonds. In spite of the very favorable coplanarity of the phosphorin and pyridine rings in **7**, such a situation is not found in our case and the two rings do not cooperate for enhancing the π-acceptor capacity of the ligand as in 2,2'-bipyridine complexes. Indeed, the C₅-C₆ bridge in **7** has exactly the same length as the C-C bridge in free 2,2'-bipyridine¹³ (1.490 (6) Å in **7** vs. 1.490 (3) Å in bpy¹³) and the lengthening of the N-C₆ bond in **7** is not significant (1.367 (5) vs. 1.346 (2) Å for the corresponding bond in bpy,¹³ much larger values being found in a molybdenum(II) complex, 1.388 (4) Å¹³). As a result of the noncooperativity between the phosphorin and pyridine units in **7**, the Cr-N bond appears to be weaker in **7** than in 2,2'-bipyridine-chromium complexes. In the latter case, typical Cr-N bond lengths are between 2.08 and 2.14 Å,¹⁴ whereas in **7**, the observed value is 2.193 (4) Å. In fact, the pyridine ring of **7** behaves as an isolated pyridine ligand. The comparison between the structural data recorded for **7** and for (py)Cr(CO)₅¹⁵ is perfectly illustrative (N-Cr-C=O (trans)): N-Cr, 2.193 (4) Å in **7**, 2.194 (4) Å in (C₅H₅N)Cr(CO)₅; Cr-C, 1.825 (5) Å in **7**, 1.824 (6) Å in (C₅H₅N)Cr(CO)₅; C=O, 1.156 (6) Å in **7**, 1.153 (5) Å in (C₅H₅N)Cr(CO)₅.

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It is well established that orbital orderings are very different for phosphorin and pyridine.¹⁶ Thus, orbitals of similar symmetries in both heterocycles have very different energies and we suspect that the noncooperativity of phosphorin and pyridine in complex **7** is merely due to a poor orbital mixing between these two subunits. Of course, full theoretical calculations are needed in order to ascertain this hypothesis.

The phosphorin unit of **1** is obviously a better ligand than 2,4,6-triphenylphosphorin as evidenced by the comparison of the P–Cr bond lengths in **7** and (2,4,6-triphenylphosphorin)pentacarbonylchromium:¹⁷ 2.280 (1) Å vs. 2.372 (4) Å. Aside from a possible chelate effect in **7**, the α, α' -diphenyl substitution of the triphenylphosphorin obviously decreases its P-ligating ability. The geometry of the phosphorin unit is perfectly normal in **7** (planar ring, equivalent C–C bond lengths) except for the extremely short P–C bond lengths (mean value 1.708 (4) Å). In free phosphorins, the P–C bond lengths are close to 1.73–1.74 Å.¹⁸ The observed shortening is very probably a consequence of the P-complexation. Indeed, Bickelhaupt¹⁹ has observed a 0.021-Å shortening of the P=C double bond of mesityl(diphenylmethylene)phosphine upon P-complexation by Cr(CO)₅.

Experimental Section

Air-sensitive materials were handled by standard argon flow techniques. Solvents were dried by standard methods and distilled before use. NMR spectra were recorded on a Bruker WP 80 spectrometer at 80.13 MHz for ¹H, 32.435 MHz for ³¹P, and 20.15 MHz for ¹³C. ³¹P chemical shifts are externally referenced to 85% H₃PO₄; ¹H and ¹³C chemical shifts are internally referenced to Me₄Si; δ is positive for downfield shifts in all cases. We thank our colleague Claude Charrier for the recording of the ¹H and ¹³C spectra and for discussion about their interpretations. IR spectra were obtained on a Perkin-Elmer 257 instrument. Elemental analyses were performed by "Service Central de Microanalyse du CNRS". Mass spectra were recorded by Mr. Charré (SNPE) on a Nermag R10-10 spectrometer using the chemical ionization (CID) or the electronic impact (EI) techniques. Chromatographic separations were performed on silica gel columns (70–230 mesh, Riedel de Haën). The preparation of **1** is described thoroughly in ref 6.

4,5-Dimethyl-2-(2-pyridiniumyl)phosphorin Chloride (2). A stream of gaseous anhydrous HCl was bubbled for 5 min through an ether solution of ligand **1** at room temperature. The clear yellow precipitate was filtered off, washed with ether, and then dried under vacuum at 50 °C. The yield was quite quantitative. An analytical sample was obtained by sublimation (160 °C, $p = 0.5$ mmHg). Anal. Calcd for C₁₂H₁₃ClNP: C, 60.64; H, 5.51; N, 5.89. Found: C, 59.49; H, 5.54; N, 5.65. IR spectrum: $\nu(\text{NH}^+)$ 2595 s, vbr cm⁻¹ (KBr disk); $\nu(\text{NH}^+)$ 2580–2600 vbr cm⁻¹ (CDCl₃). Mass spectrum (70 eV, EI): m/e 202 (18%) [M – Cl], 201 (100%) [M – HCl], 186 (92%). ¹H NMR (CDCl₃ + D₂O): δ 2.55 (s, 3 H, Me), 2.60 (d, $J(\text{H-P}) = 3.7$ Hz, 3 H, Me), 7.44 (m, 1 H, pyridine H), 8.04 (m, 2 H, pyridine H), 8.57 (d, $^3J(\text{H-P}) = 4.7$ Hz, 1 H, H–C₃), 8.57 (d, $^2J(\text{H-P}) = 40.5$ Hz, 1 H, H–C₆), 8.82 (d, $^3J(\text{H-H}) = 4.9$ Hz, 1 H, H–C₆). ³¹P NMR: δ 196.6 (CDCl₃); δ 192.4 (CDCl₃ + D₂O).

(4,5-Dimethyl-2-(2-pyridyl)phosphorin-P)pentacarbonylchromium (6) and (4,5-Dimethyl-2-(2-pyridyl)phosphorin)tetracarbonylchromium (7). (THF)Cr(CO)₅ (from 0.53 g (2.4 mmol) of Cr(CO)₆ in 150 cm³ of THF under UV irradiation for 1.5 h) and ligand **1** (0.5 g, 2.4 mmol) were stirred together for 1 h at room temperature. The solvent was removed under vacuum, and the residue was chromatographed with benzene–hexane (60:40, R_f 0.5), affording 0.75 g (85%) of **7**.

The data for **6** were recorded before the chromatographic separation. $\delta_{31\text{P}}(\text{6})$ spectrum for **6** (C₆D₆): $\nu(\text{CO})$ 2060 m, 1980 vs cm⁻¹. $\delta_{31\text{P}}(\text{6}) = 208.6$ (C₆D₆). Anal. Calcd for C₁₆H₁₂CrNO₄P (7): C, 52.61; H, 3.31; N, 3.83; P, 8.48; Cr, 14.23. Found: C, 51.62; H, 3.28; N, 4.20; P, 8.18; Cr, 13.21. IR spectrum for **7** (CHCl₃): $\nu(\text{CO})$ 2020 s, 1925 vs, br, 1865 s cm⁻¹. ¹H NMR for **7** (CDCl₃): δ 2.44 (d, $J(\text{H-P}) = 5.3$ Hz, 3 H, Me), 2.51 (s, 3 H, Me), 7.10 (m, 1 H, pyridine H), 7.85 (m, 2 H, pyridine H), 8.12 (d, $^3J(\text{H-P}) = 13.4$ Hz, 1 H, H–C₃), 8.60 (d, $^2J(\text{H-P}) = 27.34$ Hz, 1 H, H–C₆), 9.12 (d, $^3J(\text{H-H}) = 5.4$ Hz, 1 H, H–C₆). ³¹P NMR for **7** (CDCl₃): δ 249.6. Mass spectrum for **7** (CID CH₄⁺, ⁵²Cr): m/e 365 (100%) [M].

(4,5-Dimethyl-2-(2-pyridyl)phosphorin)tetracarbonyltungsten (4). The same procedure as above with W(CO)₆ (0.84 g, 2.4 mmol) and ligand **1** (0.5 g, 2.4 mmol) gives 0.55 g (46%) of **4**. Anal. Calcd for C₁₆H₁₂NO₄PW: C, 38.65; H, 2.43; N, 2.81; P, 6.23; W, 36.98. Found: C, 39.72; H, 2.48; N, 2.74; P, 6.34; W, 35.99. ¹H NMR (CDCl₃): δ 2.45 (d, $J(\text{H-P}) = 5.3$ Hz, 3 H, Me), 2.54 (s, 3 H, Me), 7.10 (m, 1 H, pyridine H), 7.95 (m, 2 H, pyridine H), 8.21 (d, $^3J(\text{H-P}) = 9.5$ Hz, 1 H, H–C₃), 8.35 (d, $^2J(\text{H-P}) = 27.1$ Hz, 1 H, H–C₆), 9.29 (dm, $^3J(\text{H-H}) = 5.6$ Hz, 1 H, H–C₆). ³¹P NMR (CDCl₃): δ 205.2 (¹J(³¹P–¹⁸³W) = 271 Hz). Mass spectrum (CID CH₄⁺, ¹⁸⁴W): m/e 497 (90%) [M], 470 (100%) [M + H – CO]. IR spectrum (CHCl₃): $\nu(\text{CO})$ 2024 s, 1923 vs, br, 1865 s cm⁻¹.

(4,5-Dimethyl-2-(2-pyridyl)phosphorin)tetracarbonylmolybdenum (8). Mo(CO)₆ (0.28 g, 1.1 mmol) and **1** (0.2 g, 1.0 mmol) were heated at 155 °C for 19 h in a sealed tube. The orange-red crystals were chromatographed with toluene (R_f 0.5), affording 0.35 g (85%) of bright orange crystals of **8**, mp (Et₂O) 195–196 °C. Anal. Calcd for C₁₆H₁₂MoNO₄P: C, 46.96; H, 2.95; N, 3.42; P, 7.56; Mo, 23.44. Found: C, 47.17; H, 3.21; N, 2.85; P, 7.36; IR spectrum (CHCl₃): $\nu(\text{CO})$ 2028 s, 1934 vs, 1870 s cm⁻¹. Mass spectrum (70 eV, ⁹⁸Mo, EI): m/e 411 (4%) [M], 383 (3%) [M – CO], 355 (2.5%) [M – 2 CO], 327 (3%) [M – 3 CO], 299 (21%) [M – 4 CO], 201 (100%) [L]. ¹H NMR ((CD₃)₂CO): δ 2.50 (d, $J(\text{H-P}) = 5.3$ Hz, Me), 2.58 (d, $J(\text{H-P}) = 1.9$ Hz, Me), 7.40 (m, 1 H, H–C₃), 8.07 (m, 1 H, H–C₄), 8.46 (m, 1 H, H–C₃), 8.61 (d, $^3J(\text{H-P}) = 14.2$ Hz, 1 H, H–C₃), 8.69 (d, $^2J(\text{H-P}) = 26.6$ Hz, 1 H, H–C₆), 9.18 (dm, $^3J(\text{H-H}) = 5.6$ Hz, 1 H, H–C₆). ³¹P NMR (CDCl₃): δ 220.0.

X-ray Data Collection and Processing. Suitable red single crystals of **7** were obtained by slow evaporation of THF solutions at room temperature.

A systematic search in reciprocal space using a Philips PW1100/16 automatic diffractometer showed that crystals of **7** belong to the monoclinic system.

The unit-cell dimensions and their standard deviations were obtained and refined at room temperature with Cu K α radiation ($\lambda = 1.5418$ Å) by using 25 carefully selected reflections and the standard Philips software. Final results: C₁₆H₁₂NO₄PCr, mol wt 365, $a = 12.955$ (5) Å, $b = 18.943$ (8) Å, $c = 6.635$ (3) Å, $\beta = 91.83$ (2)°, $V = 1627$ Å³, $Z = 4$, $d_{\text{calcd}} = 1.491$ g cm⁻³, $d_{\text{obsd}} = 1.47 \pm 0.02$ g cm⁻³, $\mu = 69.92$ cm⁻¹, $F_{000} = 744$, space group P2₁/n.

A parallelepipedic crystal of dimensions 0.02 × 0.11 × 0.16 mm was sealed in a Lindemann glass capillary and mounted on a rotation-free goniometer head. All quantitative data were obtained from a Philips PW1100/16 four-circle automatic diffractometer, controlled by a P852 computer, using graphite-monochromated radiation and standard software. The vertical and horizontal apertures in front of the scintillation counter were adjusted so as to minimize the background counts without loss of net peak intensity at the 2 σ level. The total scan width in the $\theta/2\theta$ flying step-scan used was $\Delta\theta = 0.9 + (\text{Cu}, \text{K}\alpha_1, \alpha_2 \text{ splitting})^\circ$ with a step width of 0.04° and a scan speed of 0.016° s⁻¹. A total of 2342 hkl and $hk\bar{l}$ reflections were recorded ($5^\circ < \theta < 57^\circ$). The resulting data set was transferred to a PDP 11/60 computer, and for all subsequent computations, the Enraf-Nonius SDP/V18 package was used²⁰ with the exception of a local data-reduction program.

Three standard reflections measured every hour during the entire data-collection period showed no significant trend.

The raw step-scan data were converted to intensities with use of the Lehmann–Larson method²¹ and then corrected for Lorentz, po-

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larization, and absorption factors, the last computed by the numerical integration method of Busing and Levy²² (transmission factors between 0.26 and 0.77). The diffraction power of the crystal was poor, and weak reflections were not precise enough to allow keeping data below 3σ , so a unique data set of 1640 reflections having $I > 3\sigma(I)$ was used for determining and refining the structure.

The structure was solved with use of the heavy-atom method. After refinement of the heavy atoms, a difference-Fourier map revealed maxima of residual electronic density close to the positions expected for hydrogen atoms. They were introduced in structure factor calculations by their computed coordinates ($C-H = 0.95 \text{ \AA}$) and isotropic temperature factors of 6 \AA^2 but not refined. Full least-squares refinement converged to $R(F) = 0.075$ and $R_w(F) = 0.096$ [$w = 1/\sigma_{\text{count}}^2 + (pI)^2$]. The ignorance factor p was estimated from equivalent $0kl$ and $0k\bar{l}$ intensities; for $p = 0.08$ the unit-weight observation is equal to 1.93. A final difference map revealed no significant maxima. The scattering factors of Cromer and Waber²³ and the anomalous dis-

persion coefficients of Cromer²⁴ were used in all structure factor calculations.

Registry No. 1, 82884-19-3; 2, 91606-21-2; 3, 91606-16-5; 4, 91606-17-6; 5, 89161-57-9; 6, 91606-18-7; 7, 91606-19-8; 8, 91606-20-1; (THF)Cr(CO)₅, 15038-41-2; W(CO)₆, 14040-11-0; Mo(CO)₆, 13939-06-5.

Supplementary Material Available: Table IV, positional and thermal parameters for hydrogen atoms, Table V, least-squares mean planes of interest, Table VI, thermal parameters for anisotropic atoms, and Table VII, observed and calculated structure factor amplitudes for all observed reflections ($\times 10$) (11 pages). Ordering information is given on any current masthead page.

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Monomeric and Anion-Bridged Dimeric and Polymeric Oxamide Oxime Complexes of Copper(II): Preparation, Crystal and Molecular Structures, and Magnetic Properties

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Aquabis(oxamide oxime)copper(II) sulfate, $[\text{Cu}(\text{C}_2\text{H}_6\text{N}_4\text{O}_2)_2(\text{H}_2\text{O})]\text{SO}_4$, crystallizes in the orthorhombic space group $Pbca$ (D_{2h}^8) with 8 molecules in a unit cell of dimensions $a = 7.829$ (2) \AA , $b = 12.568$ (4) \AA , and $c = 28.284$ (12) \AA . The structure has been refined by least-squares methods to an R_w of 0.031 for 1320 reflections. The copper ion is coordinated by four oxime nitrogen atoms and the water molecule in a square-pyramidal arrangement. The complex molecules are monomeric, and the magnetic susceptibility data obey the Curie-Weiss law $\chi = C/(T - \Theta)$ with $C = 0.442$ (1) and $\Theta = 0.68$ (1)°.

Bis(μ -sulfato)bis[aqua(oxamide oxime)copper(II)], $[\text{Cu}(\text{C}_2\text{H}_6\text{N}_4\text{O}_2)(\text{H}_2\text{O})(\text{SO}_4)]_2$, crystallizes in the triclinic space group $P\bar{1}$ with 1 molecule in a unit cell of dimensions $a = 6.726$ (1) \AA , $b = 7.982$ (1) \AA , $c = 9.462$ \AA , $\alpha = 66.93$ (1)°, $\beta = 74.37$ (1)°, and $\gamma = 68.81$ (1)°. The final R_w was 0.026 for 1457 reflections. The copper(II) ions are exchange coupled in this bimetallic complex, and the magnetic susceptibility data in the temperature range 1.4–65.7 K yield a singlet-triplet splitting of 2.55 cm^{-1} , with the singlet state being the ground state. The best fit g value was 2.19.

catena- μ -Sulfato[di aqua(oxamide oxime)copper(II)], $[\text{Cu}(\text{C}_2\text{H}_6\text{N}_4\text{O}_2)(\text{H}_2\text{O})_2(\text{SO}_4)]_m$, crystallizes in the orthorhombic space group $Pcca$ (D_{2h}^8) with 4 molecules in a unit cell of dimensions $a = 7.121$ (1) \AA , $b = 9.734$ (2) \AA , $c = 13.770$ (2) \AA . The final R_w was 0.031 for 800 reflections. In the sulfato-bridged polymeric molecules, "4 + 1 + 1" distorted-octahedral coordination about copper is achieved by coordination of two nitrogens from oxamide oxime, by two oxygens from separate sulfate ions that propagate the chain, and by two water molecules. Magnetic measurements reveal antiferromagnetic exchange coupling in the unusual chain compound catena-dichloro(oxamide oxime)copper(II) with best fit parameters to the Heisenberg exchange model being $J = -1.0$ (1) cm^{-1} and $g = 2.12$ (1).

Introduction

Complexes of metal salts with α,β -dione dioximes (α,β -dodoH₂) as chelating ligands have been the object of recent interest since the nature of the complexes formed in the solid state depends on the crystallization conditions.^{1,2} Monomeric,³

dimeric,⁴⁻⁹ and polymeric chain compounds^{2,10-12} of the neutral ligand are known, and exchange coupling is frequently found in the oligomeric and polymeric compounds.¹²⁻¹⁴ For example, the dimeric compound $[\text{Cu}(\text{dimethylglyoxime})\text{Cl}_2]_2$ exhibits a triplet ground state,^{13,14} and the chain compound $[\text{Cu}(\text{diphenylethanedione dioxime})\text{Cl}_2]_n$ is an $S = 1/2$ Heisenberg antiferromagnet.¹² Compounds of charged ligands and of mixed-ligand systems have also been prepared and studied recently.¹⁵

The ligand oxamide oxime¹⁶ (oaoH₂) is of particular interest since the amino groups may also be expected to coordinate to metal ions, and in this manner polymeric compounds with short pathways for superexchange interactions may be formed. As a part of a systematic study of the coordination chemistry

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