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Supplementary Material Available: Tables of atomic (hydrogen and non-hydrogen) coordinates and temperature factors, bond lengths, bond angles, and anisotropic temperature factors for 2, 3, and 7 and tables of torsion angles for 2 and 3 (16 pages). Ordering information is given on any current masthead page.

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Structural and Electrochemical Study of a 2,2′-Biphosphinine

Pascal Le Floch, Duncan Carmichael, Louis Ricard, and François Mathey*

Laboratoire de Chimie du Phosphore et des Métaux de Transition, CNRS UM 13, DCPH, Ecole Polytechnique, 91128 Palaiseau Cedex, France

Anny Jutand and Christian Amatore*

Laboratoire de Chimie, URA CNRS 1110, Ecole Normale Supérieure, 24 rue Lhomond, 75231 Paris Cedex 05, France

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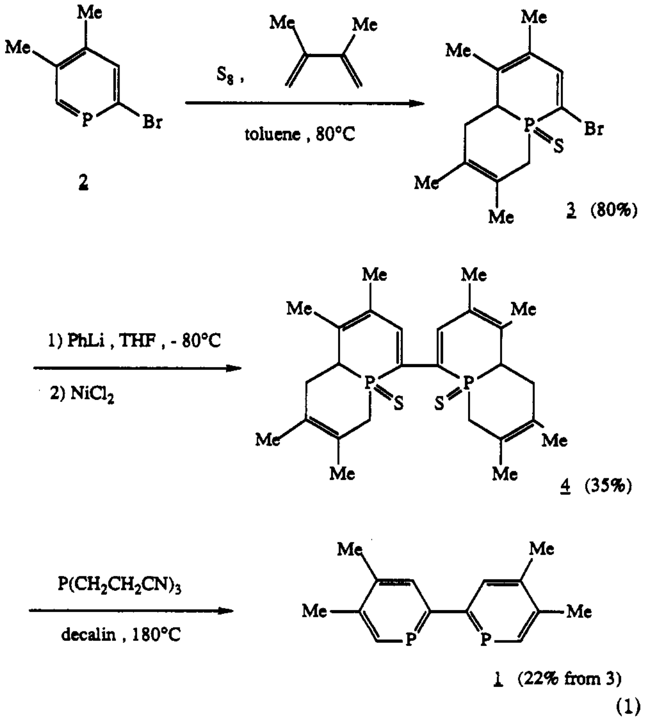
An improved synthesis of 4,4′,5,5′-tetramethyl-2,2′-biphosphinine from 2-bromo-4,5-dimethylphosphinine using $(Ph_3P)_2CoCl_2$ as the coupling reagent is described. The coupling can also be effected in the coordination sphere of molybdenum tetracarbonyl via a bromine to lithium exchange followed by C–C bond formation with $(DME)NiBr_2$. The recovery of the free 2,2′-biphosphinine from the $Mo(CO)_4$ chelate thus obtained appears to be difficult. The X-ray crystal structure analysis of the 2,2′-biphosphinine at −100 °C suggests that the interaction between the two rings and the rotation barrier around the C–C bridge are weak. The complexation with $Cr(CO)_4$ does not alter the geometry of the biphosphinine, and no electronic delocalization seems to be operative within the five-membered metallacycle. The electrochemical reduction of the tetramethylbiphosphinine is easier than that of 4,4′-dimethyl-2,2′-bipyridine. The first monoelectronic wave occurs at -1.85_2 V vs SCE in DMF for the phosphorus ligand as compared to -2.20_1 V vs SCE for the nitrogen ligand. As a consequence, the 2,2′-biphosphinine is a better ligand for electron-rich metals and is able to displace 2,2′-bipyridine from its $Cr(CO)_4$ chelate.

In a recent communication,[1] we have described the synthesis of the first 2,2′-biphosphinine 1. As the phosphorus analogues of the well-known 2,2′-bipyridines, 2,2′-biphosphinines offer some interesting perspectives on coordination chemistry. Before undertaking the study of their transition-metal complexes, however, it was necessary to evaluate the structural requirements and the donor–acceptor capacity of this new class of chelating ligands. In this work, we describe several experiments aimed at the improvement of the synthesis of 1 together with its X-ray crystal structure analysis and a comparison of its electrochemical properties with those of a related 2,2′-bipyridine.

Results and Discussion

The synthesis of 1 as reported in our preliminary communication is depicted in eq 1. After protecting the reactive P=C double bond via a [2 + 4] cycloaddition, we performed a bromine to lithium exchange and subsequently coupled the resulting lithio derivative with nickel(II) chloride, thereby obtaining 4. A reductive [2 + 4] cycloreversion then led to the 2,2′-biphosphinine 1. The weak point of this scheme was clearly the coupling step, since other experiments demonstrated that the bromine to lithium exchange is instantaneous and almost quantitative.[2] Thus, we tried the several coupling reagents shown in eq 2 while retaining all other reagents and experimental conditions. Bis(triphenylphosphine)di-



(1)

$$3 \xrightarrow[\text{(3) } P(CH_2CH_2CN)_3\text{, decalin, 180 °C, 7 h}]{\text{(1) PhLi, THF, −80 °C (2) } MX_2\text{, −80 °C, room temp}} 1 \qquad (2)$$

MX_2 = $(Ph_3P)_2NiCl_2$ (25%), $(Bu_3P)_2NiCl_2$ (0%), $(DME)NiBr_2$ (30%), $CoCl_2$ (10%), $(Ph_3P)_2CoCl_2$ (48%)

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[1] Le Floch, P.; Carmichael, D.; Richard, L.; Mathey, F. *J. Am. Chem. Soc.* 1991, *113*, 667.

[2] Le Floch, P.; Carmichael, D.; Mathey, F. *Organometallics* 1991, *10*, 2432.

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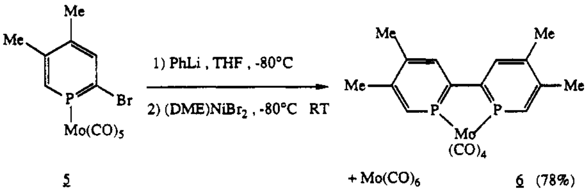
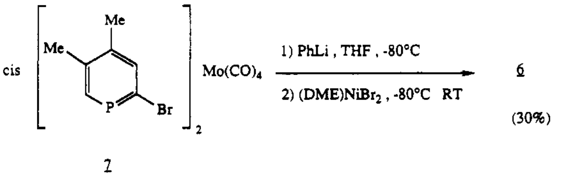
chlorocobalt dramatically improved the overall yield of biphosphinine and is now used routinely.

Another approach was also tested. In a preceding work,[2] we demonstrated that it is also possible to perform the bromine to lithium exchange on a 2-bromophosphinine–$W(CO)_5$ complex. It was tempting to use the resulting 2-lithiophosphinine complexes to create the C–C bridge. Among all the coupling reagents used above, only $(DME)NiBr_2$[3] proved to be useful. The coupling was attempted on 2-bromophosphinine–$Mo(CO)_5$ and *cis*-bis(2-bromophosphinine)–$Mo(CO)_4$ complexes synthesized by reaction of 2-bromophosphinine with $Mo(CO)_6$ (see Experimental Section). Curiously, the coupling is far more efficient in the first case (eqs 3 and 4). Unfortunately, to date, we have been unable to recover the free biphosphinine 1 from its $Mo(CO)_4$ chelate using the already described decomplexation techniques.[2]



(3)



(4)

In order to quantify the effect of complexation upon the biphosphinine system, we decided to carry out a low-temperature X-ray crystal structure analysis of 1. The structural parameters as obtained at −100 °C are summarized in Table I and compared[11] to those of the corresponding $Cr(CO)_4$ chelate.[1] The asymmetric unit contains two molecules of 1, one with a transoid (Figure 2) and the other with a cisoid geometry (Figure 3) . The only significant difference between the cisoid and transoid molecules is observed on the $P–C_\alpha–C_\alpha$ angle, which is smaller in the cisoid conformation. This is probably a result of the increase of the steric repulsion between the two rings with a decrease of the interplane angle. The comparison of the two molecules shows no influence of the angle between the two ring planes on the structure of each ring, suggesting that no special conjugative interaction exists between the two subunits and, as a consequence, that the barrier against the rotation of the two rings around the C–C bridge is weak. The two conformations existing in the solid are probably blocked by the packing forces of the crystal, and in solution, we have never observed any sign of restricted rotation by NMR spectroscopy, at 25 °C.

The effect of complexation onto the structure of biphosphinine is negligible. Apart from a slight shortening of the bridge which is perhaps not significant, we observe only the classical rehybridization at phosphorus upon complexation of the lone pair, where a decrease of Coulombic repulsion leads to a widening of the $\angle C_\alpha PC_{\alpha'}$ angle from ca. 100.5 to 104.3°. In contrast to our earlier expectation,[1] it is clear that no delocalization takes place

Table I. Structural Comparison of 2,2′-Biphosphinine and Its $Cr(CO)_4$ Complex

bond length (Å) or angle (deg)	2,2′-bisphosphinine			$Cr(CO)_4$ complex[1]
	transoid			
	P_1	P_8	cisoid	
$P–C_\alpha$ (internal)	1.731 (4)	1.740 (5)	1.736 (4)	1.737 (2)
$P–C_\alpha'$ (external)	1.715 (4)	1.720 (4)	1.716 (5)	1.711 (3)
$C_\alpha–C_\beta$	1.401 (4)	1.399 (4)	1.388 (6)	1.392 (3)
$C_\beta–C_\gamma$	1.380 (6)	1.395 (6)	1.396 (6)	1.395 (4)
C_α'-C_β'	1.396 (4)	1.395 (5)	1.386 (6)	1.385 (4)
C_β'-C_γ	1.401 (7)	1.396 (7)	1.392 (6)	1.400 (3)
$C_\alpha–C_\alpha$ (bridge)	1.484 (6)		1.490 (8)	1.467 (3)
$C_\alpha–P–C_\alpha'$	100.7 (2)	100.9 (2)	100.2 (2)	104.3 (1)
$P–C_\alpha–C_\alpha$	118.6 (2)	120.0 (2)	115.6 (2)	113.7 (2)
interplane angle	148.74 ± 0.08		46.59 ± 0.42	0.02 ± 0.40

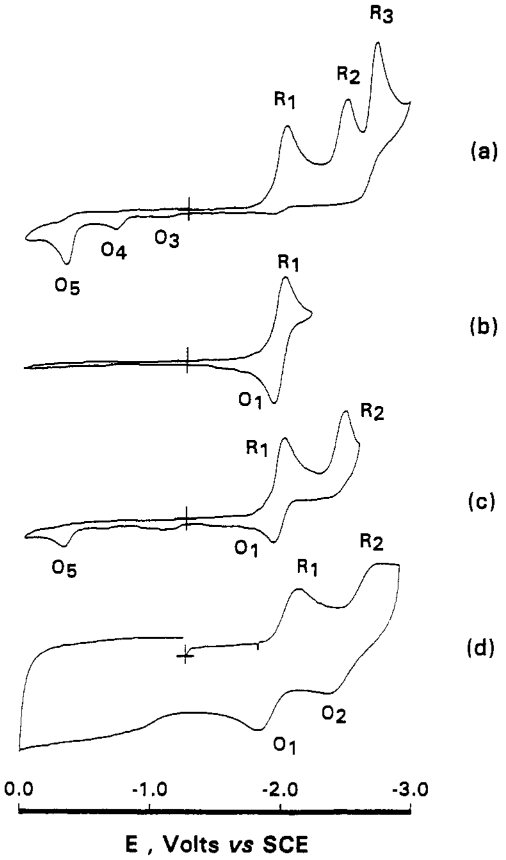


Figure 1. Cyclic voltammograms of 1 (2 mM in DMF, 0.3 M nBu_4NBF_4, 20 °C) at a gold-disk electrode (diameter 0.5 mm in (a–c) and 0.125 mm in (d)). Scan rate: (a–c) 0.2 V s^{-1}; (d) 2000 V s^{-1}.

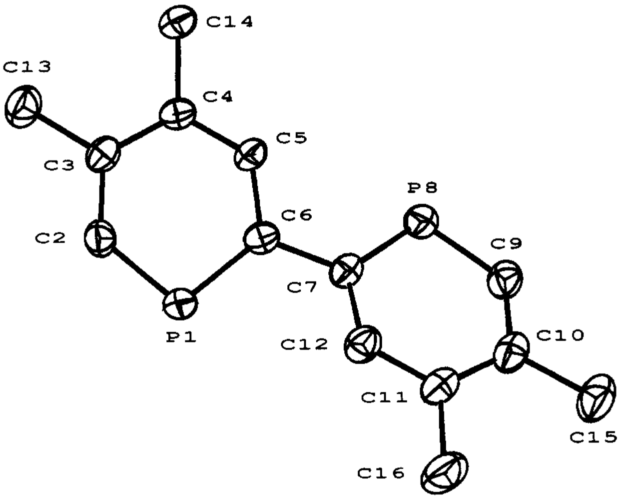


Figure 2. Molecule of 1 with a transoid geometry.

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(4) (a) Fischer, W.; Hellner, E. *Tetrahedron Lett.* **1968**, 6227. (b) Bart, J. C. J.; Daly, J. J. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 811.

(5) (a) Kuzkowski, R. L.; Ashe, A. J., III. *J. Mol. Spectrosc.* **1972**, *42*, 457. (b) Lattimer, R. P.; Kuzkowski, R. L.; Ashe, A. J., III. *J. Mol. Spectrosc.* **1975**, *57*, 428.

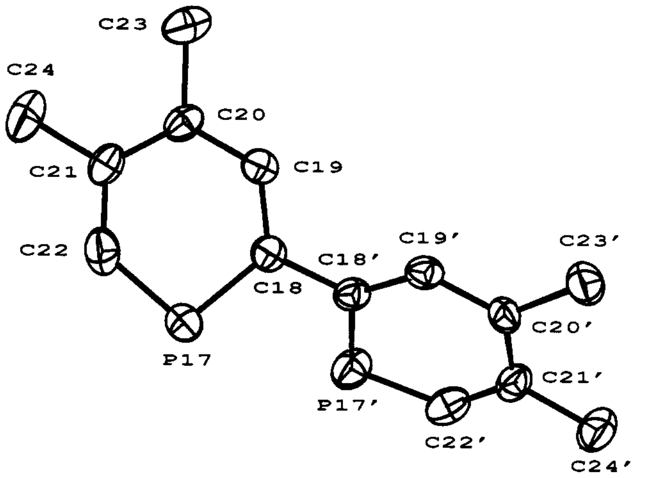

Figure 3. Molecule of 1 with a cisoid geometry.

Table II. Structural Comparison of 2,2′-Bipyridine and Its $Cr(CO)_4$ Complex

bond length (Å)	bpy[3]	$Cr(CO)_4$ complex[a] (this work)	
$N–C_\alpha$	1.346 (2)	1.348 (4)	1.350 (5)
$N–C_\alpha'$	1.341 (2)	1.347 (4)	1.341 (4)
$C_\alpha–C_\beta$	1.394 (2)	1.378 (6)	1.398 (5)
$C_\beta–C_\gamma$	1.385 (2)	1.375 (6)	1.376 (7)
$C_\alpha'–C_\beta'$	1.384 (2)	1.373 (6)	1.379 (6)
$C_\beta'–C_\gamma$	1.383 (3)	1.381 (7)	1.361 (8)
$C_\alpha–C_\alpha$	1.490 (3)	1.471 (5)	

[a] N–Cr = 2.094 (3) and 2.084 (3) Å; ∠NCrN = 76.8 (1)°; Cr–(trans CO) = 1.852 (3) and 1.855 (4) Å; Cr–(cis CO) = 1.901 (3) and 1.891 (3) Å.

within the five-membered metallacycle of the $Cr(CO)_4$ complex. The situation is similar with 2,2′-bipyridine,[6] as is shown in Table II.

In order to compare the donor–acceptor properties of biphosphinines with those of the corresponding bipyridines more precisely, we decided to study the electrochemical properties of 1. The cyclic voltammetry of biphosphinine 1, in DMF solution, was performed at a stationary gold-disk electrode at a scan rate of 0.2 V s-1. 1 exhibits three reduction peaks, R_1 ($E^p = -1.88_6$ V vs SCE), R_2 ($E^p = -2.34_6$ V vs SCE), and R_3 ($E^p = -2.55_8$ V vs SCE) (Figure 1a), with three oxidation peaks, O_3 ($E^p = -1.05_2$ V vs SCE), O_4 ($E^p = -0.68_4$ V vs SCE), and O_5 ($E^p = -0.31_4$ V vs SCE), being present on the reverse scan (Figure 1a). The first reduction peak R_1 is chemically reversible at 0.2 V s^{-1} ($E^\circ_1 = -1.85_2$ V vs SCE) (Figure 1b), and determination of its absolute number of electrons[7] shows that it is a monoelectronic transfer ($n = 1.15 \pm 0.05$) which affords the monoradical anion of 1 (eq 5).

$$1 + e^- \rightarrow 1^{\bullet -} \qquad E^\circ_1 = -1.85_2 \text{ V vs SCE} \tag{5}$$

The second reduction peak R_2 is chemically irreversible at 0.2 V s^{-1} (Figure 1c) but becomes gradually reversible upon increasing the scan rate (Figure 1d), with total reversibility ($E^\circ_2 = -2.42_7$ V vs SCE) being achieved for scan rates above 2000 V s^{-1}. The similarity of the peak currents of R_1 and R_2 demonstrates that this second electron transfer is also monoelectronic (eq 6).

$$1^{\bullet -} + e^- \rightarrow 1^{2-} \qquad E^\circ_2 = -2.42_7 \text{ V vs SCE} \tag{6}$$

The third, chemically irreversible, reduction peak R_3 progressively disappears at high scan rate ($v = 2000$ V s^{-1}) concomitant with the increasing reversibility of peak R_2. This demonstrates that the species which is reduced at peak R_3 (eq 8) results from a chemical reaction of the species 1^{2-} (eq 7) formed at the second reduction peak R_2. We can therefore propose the following mechanism for the process observed at wave R_3:

$$1^{2-} \rightarrow 1^* \quad k_1 \tag{7}$$

$$1^* + ne^- \rightarrow P_1 \quad \text{wave } R_3 \tag{8}$$

Although no attempt has been made to characterize the resulting product 1*, the chemical reaction affecting 1^{2-} (eq 7) is probably a protonation since the addition of water gives rise to an increase in the peak current R_3.

The oxidation peaks O_4 and O_5 present on the reverse scan disappear with increasing scan rate (respectively at $v = 50$ and 200 V s^{-1}), while the oxidation peak O_3 first increases ($0.2 < v < 20$ V s^{-1}) and then disappears ($v > 2000$ V s^{-1}). O_3 is observed when reversing the direction of the potential scan before wave R_3 and is, therefore, the oxidation peak of the species 1* (eq 9).

$$1^* \rightarrow e^- + P_2 \quad \text{wave } O_3 \tag{9}$$

Oxidation peak O_4 is only present when the direction of the potential scan is reversed after the reduction peak R_3 and can therefore be ascribed to the oxidation of P_1 formed in eq 8.

$$P_1 \rightarrow P_3 + ne^- \quad \text{wave } O_4 \tag{10}$$

The fact that the peak current of O_5 is greater than the peak current of O_3 (Figure 1a) requires that the species which is oxidized at peak O_5 (eq 12) is not P_2 or a species formed from P_2 by a chemical reaction. Instead, it must result from the evolution of 1* (eq 11).

$$1^* \rightarrow 1^{**} \quad k_2 \tag{11}$$

$$1^{**} \rightarrow P_3 + e^- \quad \text{wave } O_5 \tag{12}$$

That the oxidation peak O_3 first disappears and then reappears upon increasing the scan rate demonstrates that the rate constant k_2 is smaller than k_1.

In order to compare the properties of this new ligand with those of analogous nitrogen derivatives, we have investigated the electrochemical properties of the related 4,4′-dimethyl-2,2′-bipyridine ligand. The cyclic voltammetry of this ligand performed under the same conditions as above presents two reduction peaks, $R_{1'}$ ($E^p = -2.20_1$ V vs SCE) and $R_{2'}$ ($E^p = -2.70_7$ V vs SCE). The first wave, which involves one electron, is chemically reversible ($E^\circ_{1'} = -2.16_4$ V vs SCE), while the second reduction peak is chemically irreversible even at scan rates above 500 V s^{-1}.

Comparison of the respective standard potentials $E^\circ_1 = -1.85$ V and $E^\circ_{1'} = -2.16$ V demonstrates that the biphosphinine ligand is more easily reduced than the bipyridine derivative (this difference is expected to be even higher for the analogous tetramethyl-substituted bipyridine). This result indicates that the biphosphinine ligand is a better π-acceptor than the corresponding bipyridine ligand.[8]

The respective values of the peak potential separation between the two first reduction waves of each ligand ($\Delta = E^{p2} - E^{p1} = 0.460$ V and $\Delta' = E^{p2'} - E^{p1'} = 0.506$ V for 1 and 4,4′-dimethyl-2,2′-bipyridine, respectively) indicate that the delocalizations in the corresponding radical an-

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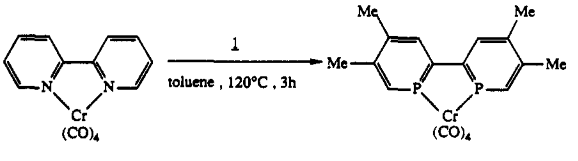
[6] Chisholm, M. H.; Huffman, J. C.; Rothwell, I. P.; Bradley, P. G.; Kress, N.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 4945.

[7] Amatore, C.; Azzabi, M.; Calas, P.; Jutand, A.; Lefrou, C.; Rollin, Y. *J. Electroanal. Chem. Interfacial Electrochem.* **1990**, *288*, 45.

[8] Ashe, A. J., III *Acc. Chem. Res.* **1978**, *11*, 153.

ions[9] are small and are nearly the same, provided that the interatomic distances between the two heteroatoms are not very different.

The fact that 2,2′-biphosphinines are substantially better π-acceptors than 2,2′-bipyridines led us to suppose that 2,2′-biphosphinines would bind more strongly low-valent metallic centers than do 2,2′-bipyridines. The assumption has been unambiguously established by the displacement reaction depicted in eq 13.



(13)

(69%, isolated yield)

To summarize, 2,2′-biphosphinines can be considered as "super-2,2′-bipyridines" for low-valent soft metals.

Experimental Section

All reactions were carried out under nitrogen, and silica gel (70–230 mesh) was used for chromatographic separations. NMR spectra were recorded on a Bruker AC-200 SY spectrometer operating at 200.13 MHz for ^{1}H, 50.32 MHz for ^{13}C, and 81.01 MHz for ^{31}P. Chemical shifts are expressed in parts per million downfield from internal TMS (^{1}H and ^{13}C) and external 85% H_3PO_4 (^{31}P). Mass spectra were obtained at 70 eV with a Shimadzu GC-MS QP 1000 spectrometer by the direct inlet method. Elemental analyses were performed by the "Service d'analyse du CNRS", at Gif-sur-Yvette, France.

4,4′,5,5′-Tetramethyl-2,2′-biphosphinine (1). Phenyllithium (31.5 mL, 2 M in 1/1 cyclohexane/ether) was added at −78 °C to a solution of sulfide 3 (20 g, 6.3×10^{-2} mol) in 150 mL of dry THF. After 5 min $(PPh_3)_2CoCl_2$ (24.7 g, 3.8×10^{-2} mol) was added and the reaction mixture was slowly warmed to room temperature (4 h). After evaporation of the solvent, the black residue was chromatographed. A first fraction with hexane/ether as eluent gave PPh_3, and a second eluted with pure ether gave a mixture of sulfide 4 and a small amount of Ph_3PO. This mixture was heated at 180 °C for 7 h with $P(CH_2CH_2CN)_3$ (12.16 g, 6.3×10^{-2} mol) in 100 mL of decalin. Chromatography of the crude reaction mixture with hexane as eluent gave 1: yield 3.72 g (48% from 3).

(4,5-Dimethyl-2-bromophosphinine)pentacarbonylmolybdenum (5) and *cis*-Bis(4,5-dimethyl-2-bromophosphinine)tetracarbonylmolybdenum (7). 4,5-Dimethyl-2-bromophosphinine (10 g, 5×10^{-2} mol) was heated with $Mo(CO)_6$ (52.8 g, 0.2 mol) in 250 mL of dry toluene at 120 °C for 5 h. After the mixture was cooled, the solvent was evaporated and the residue was chromatographed. The first fraction, eluted with hexane, afforded an excess of $Mo(CO)_6$, and the second, eluted with hexane/CH_2Cl_2 (9/1), gave 5. Yield: 16.26 g (75%). The third fraction, eluted with hexane/CH_2Cl_2 (4/1), gave 7. Yield: 3 g (20% from the starting compound).

Complex 7 can also be prepared by heating 4,5-dimethyl-2-bromophosphinine (10 g, 5×10^{-2} mol) with $Mo(CO)_6$ (7.84 g, 3×10^{-2} mol) at 120 °C for 5 h in 100 mL of dry toluene. Yield: 13.63 g (90%).

5: Yellow solid; mp 88 °C; ^{31}P NMR (CH_2Cl_2) δ 194.83 ppm; ^{1}H NMR ($CDCl_3$) δ 2.41 (s, 3 H, Me), 2.44 (s, 3 H, Me), 8.06 (s, 1 H, H_3), 8.16 (d, ^2J(H–P) = 14.35 Hz, H_6) ppm; ^{13}C NMR ($CDCl_3$) δ 21.98 (d, J(C–P) = 2.7 Hz, Me), 23.06 (d, J(C–P) = 9.6, Me), 139.27 (d, ^1J(C–P) = 23.9, C_2), 142.63 (d, ^2J(C–P) = 11.71, C_3), 145.1–146.0 (d, C_4 and C_5), 156.72 (d, ^1J(C–P) = 8.74, C_6), 203.57 (d, ^2J(C–P) = 11.69, CO cis), 209.28 (d, ^2J(C–P) = 33.26, CO trans) ppm. Anal. Calcd for $C_{12}H_8O_4PBrMO$: C, 32.83; H, 1.83. Found: C, 33.15; H, 1.7.

7: orange solid; mp 130 °C; IR (Nujol) ν(CO) 2030 (s), 1940 (vs), 1925 (br); ^{31}P NMR (CH_2Cl_2) δ 200.86 ppm; ^{1}H NMR ($CDCl_3$) δ 2.36–2.38 (m, 12 H, 4 Me), 8.04–8.16 (m, 4 H, H_3, $H_{3'}$, H_6, $H_{6'}$) ppm; ^{13}C NMR ($CDCl_3$) δ 21.95 (s, Me), 23.09 (s, Me), 138.12 (AXX′, $|^1J(C{-}P_A) + {}^3J(C{-}P_B)|$ = 23.8 Hz, C_2, $C_{2'}$), 142.37 (AXX′, $|^2J(C{-}P_A) + {}^4J(C{-}P_B)|$ = 12.7, C_3, $C_{3'}$), 145.15 (AXX′, $\sum J$(C–P) = 15.57, C_4, C_4' or C_5, $C_{5'}$), 145.48 (s, $\sum J$(C–P) = O, C_5, C_5' or C_4, $C_{4'}$), 152.55 (AXX′, $|^1J(C{-}P_A) + {}^3J(C{-}P_B)|$ = 9.8, C_6, $C_{6'}$), 205.97 (AX_2, ^2J(C–P) = 22.28, CO eq), 211.82 (AX_2, ^2J(C–P) = 22.67, CO ax) ppm. Anal. Calcd for $C_{18}H_{16}O_4P_2Br_2Mo$: C, 35.2; H, 2.62. Found: C, 35.58; H, 2.46.

(4,4′,5,5′-Tetramethyl-2,2′-biphosphinine)tetracarbonylmolybdenum (6). Phenyllithium (1.15×10^{-2} mol, 2 M in 1/1 cyclohexane/ether) was added to a solution of complex 5 (5 g, 1.14×10^{-2} mol) in 30 mL of dry THF at −78 °C. After 2 min, $NiBr_2$(DME) (2.27 g, 7.34×10^{-3} mol) was added and the reaction mixture was warmed slowly (3 h) to room temperature. After evaporation of the solvent, the crude mixture was chromatographed with hexane as eluent to remove $Mo(CO)_6$ and, finally, complex 6 was eluted with CH_2Cl_2/hexane (5/1). Yield: 2 g (78%).

6: orange solid; mp 250 °C; IR (Nujol) ν (CO) 2030 (s), 1935 (vs), 1900 (br); ^{31}P NMR (THF) δ 202.28 ppm; ^{1}H NMR δ 2.49–2.51 (m, 12 H, 4 Me), 8.27 (AXX′, 2 H, H_3, $H_{3'}$), 8.34 (AXX′, 2 H, H_6, $H_{6'}$) ppm; mass spectrum m/z (relative intensity) 454 (m, 9), 426 (M − CO, 13), 398 (M − 2CO, 7), 370 (M − 3CO, 13), 346 (M − 4CO, 90), 246 (M − $Mo(CO)_4$, 58). Anal. Calcd for $C_{18}H_{16}O_4P_2Mo$: C, 47.6; H, 3.55. Found: C, 47.33; H, 3.55.

Electrochemical Study of 1. Transient cyclic voltammetry was performed in ca. 12-mL three-electrode airtight cell connected to a Schlenk line. The working electrode consisted of a gold disk of 0.5- or 0.125-mm diameter made from a cross-section of a gold wire (Goodfellow) sealed in glass. The reference electrode was a SCE (Tacussel), separated from the solution by a bridge (3 mL) filled with a 0.3 M solution of nBu_4NBF_4 in DMF identical with that used in the cell. The counter electrode was a platinum spiral of ca. 1-cm^2 apparent surface located within 5 mm of the working electrode and facing it. A home-built potentiostat equipped with positive feedback for Ohmic-drop compensation[10] was used. The potential wave form signal generator was a Tacussel GSTP4 instrument. The voltammograms were recorded with a Nicolet 3091 digital oscilloscope and the measurements performed on the stored curves. The cyclic voltammetric measurements were performed on 2 mM solutions of the different ligands. The absolute number of electrons was determined according to a recent procedure described in ref 4.

X-ray Structure Determinations. Data were collected on an Enraf-Nonius CAD4 diffractometer with Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. The crystal structures were solved and refined using the Enraf-Nonius SDP package. In both cases, the structures were solved by direct methods. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement, while anisotropic temperature factors were used for all other atoms.

Crystals of 1, $C_{14}H_{16}P_2$, were grown from a melt (72 °C) of the compound. The product crystallizes in space group $C2/c$, with a = 22.623 (2) Å, b = 13.744 (1) Å, c = 14.371 (1) Å, β = 117.78 (1)°, V = 3953.31 (1.27) Å^3, Z = 12, d(calc) = 1.241 g/cm^3, μ = 2.9 cm^{-1}, and F(000) = 1560; the temperature for data collection was −100 ± 0.5 °C. A total of 5971 unique reflections were recorded in the range $2° \le 2\theta \le 60.0°$, of which 4188 were considered as unobserved ($F^2 < 3.0\sigma(F^2)$), leaving 1783 for solution and refinement. A non-Poisson weighting scheme was applied with a p factor equal to 0.08. The final agreement factors were R = 0.044, R_w = 0.057, and GOF = 1.09.

Crystals of $C_{14}H_8CrN_2O_4$ were obtained from a dichloromethane solution of the complex. The compound crystallizes in space group Pn, a nonstandard setting of space group Pc, with a = 8.813 (1) Å, b = 6.424 (1) Å, c = 12.522 (1) Å, β = 107.72 (1)°, V = 675.30 (27) Å^3, Z = 2, d(calc) = 1.585 g/cm^3, μ = 8.4 cm^{-1}, and F(000) = 328; the temperature for data collection was 20 ± 1 °C. A total of 1963 unique reflections were recorded in the range $2° \le 2\theta \le 60.0°$, and 1652 observed data were used for solution and re-

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finement. The final R factors were $R = 0.029$, $R_w = 0.040$, $p = 0.06$, and GOF = 1.02.

Registry No. 1, 131104-93-3; 2, 129117-81-3; 3, 131104-89-7; 4, 131104-92-2; 5, 141397-75-3; 6, 141397-76-4; 7, 141411-07-6; $Cr(bpy)(CO)_4$, 15668-63-0; $(PPh_3)_2CoCl_2$, 14126-40-0; $NiBr_2(DME)$, 28923-39-9; (4,4′,5,5′-tetramethyl-2,2′-biphosphinine)tetracarbonylchromium, 131104-94-4.

Supplementary Material Available: X-ray structure determination for 1, including tables of crystal data, positional parameters, bond distances and angles for all non-hydrogen atoms, β_{ij} values, least-squares planes, and torsion angles (7 pages). Ordering information is given on any current masthead page.

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Photochemical Synthesis and Stereodynamic Behavior of Alkoxy-Bridged (Silylene)(germylene)iron Complexes

Julian R. Koe, Hiromi Tobita, and Hiroshi Ogino*

Department of Chemistry, Faculty of Science, Tohoku University, Aoba-ku, Sendai 980, Japan

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Mixed (silylene)(germylene)iron complexes have been synthesized for the first time and are internally stabilized by a donor bridging alkoxy group: [Cp′(CO)Fe{GeMe$_2$--O(R)--SiMe$_2$}] (Cp′= C$_5$Me$_5$; R = Me, Bu^t). Two-dimensional and variable-temperature ^{1}H NMR spectroscopies establish germylene–methyl group exchange. Computer simulation of the spectra and calculation using the Eyring equation yield values for $\Delta G^{\ddagger}_{298}$ for the process of 62 kJ mol^{-1} (R = Me) and 61 kJ mol^{-1} (R = Bu^t). A mechanism involving cleavage of the Ge--O partial bond, followed by rotation of the resulting coordinated germylene moiety about the Fe═Ge double bond, is proposed for this exchange. The (silylene)(germylene)iron complexes are weighted toward the (methoxysilyl)(germylene) form, indicating that germylene ligands are more stable than their silicon analogues.

Introduction

Silylenes, well-known as reactive intermediates from their reactions with various trapping agents such as 1,3-butadiene and trimethylsilane,[1] remain, as yet, elusive, though their coordination chemistry is an area of stimulating and imaginative research. A number of unstable silylene complexes have been proposed as the intermediates of various reactions. Photochemical rearrangement of (disilanyl)carbonyliron complexes such as $CpFe(CO)_2SiMe_2SiMe_3$ (Cp = C_5H_5) reported by Pannell[2] and us[3] is one of the most well-defined reactions generating silylene-coordinated intermediates. Donor-stabilized silylene-metal complexes have been synthesized,[4–9] and more recently, reports have come describing cationic donor-free silylene complexes.[10] Another recently reported complex is a fluxional gold complex which has been described in terms of a coordinated silylene.[11] Germylene complexes are somewhat more stable, and there are consequently more reports concerning the synthesis and characterization of both base-stabilized[12] and base-free[12–14] species, including recently a paper describing exchange of moieties on a germyl group in a rhenium complex, probably via dissociation of a triflate group from the germyl group and rotation of the resulting germylene about the rhenium–germanium double bond.[15] Pannell recently reported the photolysis of (silylgermyl)- and (germylsilyl)iron complexes generating an equilibrium mixture of (silyl)(germylene) and (germyl)(silylene) intermediates and estimated the relative stability between silylene complexes and germylene com-

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