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Novel Cationic Chiral Phosphorus Ligands and Their Zwitterionic Hydridocarbonylferrate Complexes

Jean-Jacques Brunet,* Remi Chauvin,* Gérard Commenges,
Bruno Donnadieu, and Pascale Leglaye

Laboratoire de Chimie de Coordination du CNRS, Unité No. 8241, liée par conventions à l'Université Paul Sabatier et à l'Institut National Polytechnique, 205 route de Narbonne, 31077 Toulouse Cedex, France

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Summary: The reaction of (−)-N,N-dimethylephedrinium salts with R_2PNMe_2 derivatives allows the high-yield synthesis of new chiral phosphorus ligands with an ammonium side chain, termed "ephosiums". Diphenyl-N,N-dimethylephosium hexaflurophosphate reacts with $KHFe(CO)_4$ to afford the chiral zwitterionic complex diphenyl-N,N-dimethylephosium hydridotricarbonylferrate, characterized by X-ray diffraction and NMR studies.

The hydride transfer ability of mononuclear anionic group VI or VIII transition-metal complexes $[HM(CO)_n]^-$ has been established.[1,2] It has been shown that substitution of a carbonyl ligand by a phosphorus ligand generally increases the hydridic character of the resulting $[HM(CO)_{n-1}P]^-$ species.[3] An asymmetric version of this reactivity could be based either on a tight chiral ion pairing or on the use of chiral chelating ligands (P_2*). The anionic nature of the hydridometalates suggests that a hybrid method, based on a putative zwitterionic control of asymmetry transfer in a cyclic transition state (Figure 1), should be possible.

In order to perform catalysis in aqueous media, ionic ligands (usually anionic) have attracted a great deal of interest[4] and ammonium−phosphorus ligands (amphos) have been complexed at neutral transition-metal centers.[5] On the other hand, several phosphorus derivatives of ephedrine are efficient chiral auxiliaries (the chelating strategy)[6] and *N*,*N*-dialkylephedrinium salts are asymmmetric phase transfer reagents (the ion-pairing strategy).[7] We report here access to a new family of chiral phosphorus ligands derived from ephedrine, termed as "R^1,R^2-*N*,*N*-R^3,R^4-ephosium", R^1 and R^2 denoting the substituents at phosphorus (Figure 2), and their hydridocarbonylferrate complexes.

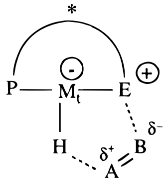


Figure 1. Possible chiral zwitterionic control for the reduction of a dipolar substrate (e.g. a prochiral ketone).

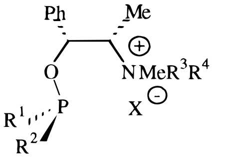
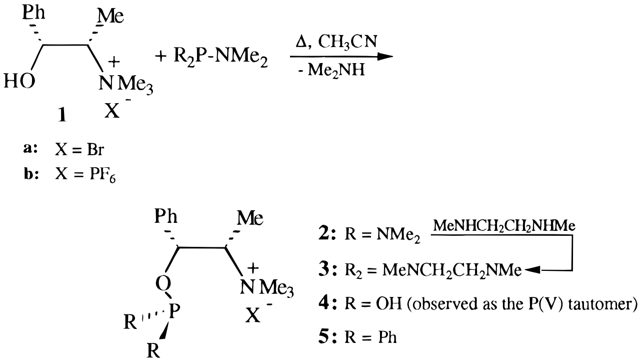


Figure 2. Nomenclature of ephosium ligands.

Scheme 1. Preparation of "R,R-*N*,*N*-dimethylephosium"



The ephosium ligands are prepared from (−)-*N*,*N*-dimethylephedrinium salts **1** according to Scheme 1.

The bis(dimethylamino)-*N*,*N*-dimethylephosium species **2a** is obtained quantitatively,[8] but its P−N bonds are very sensitive to moisture and alcohols. The hydrolysis product has been identified as O═PH(OR*)(OH), the tautomer of the corresponding dihydroxy-*N*,*N*-dimethylephosium compound **4**.[9] In order to stabilize

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[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1996.

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[6] (a) Jugé, S.; Stephan, M.; Merdès, R.; Genet, J. P.; Halut-Desportes, S. *J. Chem. Soc., Chem. Commun.* **1993**, 531. (b) Alexakis, A.; Frutos, J.; Mangeney, P. *Tetrahedron: Asymmetry* **1993**, *4*, 2427. The diphenylphosphinite of ephedrine ("ephos": Denis, P.; Mortreux, A.; Petit, F.; Buono, G.; Peiffer, G. *J. Org. Chem.* **1984**, *49*, 5276) and the N,P-rhodium chelate (*R*,*S*)-$[\{Ph_2POCHPhCHMeNMe_2\}Rh(cod)]^+$-$PF_6^-$ (Chauvin, R. Ph.D. Dissertation, Université Paris-Sud, Orsay, France, 1988) have been described.

[7] O'Donnell, M. J. in *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: Weinheim, Germany, 1993; p 389, and references therein.

[8] NMR data for **2a** in DMSO-d_6: ^{31}P (162 MHz) δ (ppm) +140.0. Procedure and full spectroscopic data available in the Supporting Information.

[9] NMR data for **4a** in DMSO-d_6: ^{31}P (81 MHz) δ (ppm) 3.8 (dd, ^1J(P,H) = 592.8 Hz, ^3J(P,H) = 9.7 Hz). Procedure and full spectroscopic data available in the Supporting Information.

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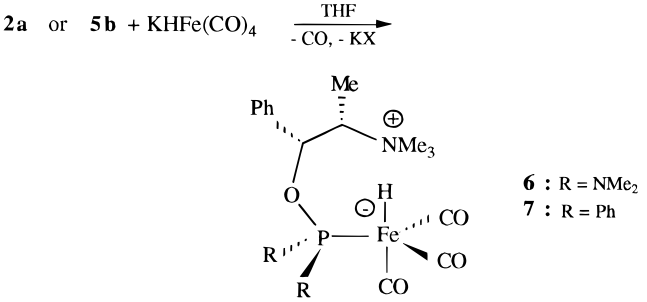
Scheme 2. Zwitterionic Ephosium Hydridotricarbonylferrates



the P—N bonds inside a diazaphospholidine ring, the ephosium **3a** has been prepared by transamidification of **2a** by *N*,*N'*-dimethylethylenediamine in refluxing acetonitrile (91% for the two steps).[10] However, the P—N bonds of **3a** turned out to be as sensitive as those of **2a**. Attempts to prepare the diphenyl-*N*,*N*-dimethylephosium species **5a** by reacting Ph_2PX derivatives with **1a** under a variety of conditions were unsuccessful. However, reacting Ph_2PNMe_2 with the more lipophilic and non-nucleophilic hexafluorophosphate **1b** afforded **5b** in 82% yield.[11]

Zwitterionic transition-metal complexes containing phosphorus ligands with either $M^+{-}L^-$ or $M^-{-}L^+$ polarity have been reported,[12] and chiral examples are now described (Scheme 2). These complexes are prepared by reacting $KHFe(CO)_4$ with the ephosium salt **2a** or **5b** in THF.

The zwitterionic complex **6** (56%) is moisture sensitive.[13] Symmetry arguments suggest that the IR spectrum in THF is consistent with a *cis*-P—Fe—H geometry, but this is not clearly confirmed from NMR data in DMSO-d_6 by simple analogy with known trends for nonzwitterionic (phosphane)hydridotricarbonylferrate complexes:[13] although the ^2J(H,P) coupling constant does not vary with temperature (20−60 °C), it is very small,[14] and the three carbonyl carbons are equivalent on the ^{13}C NMR time scale; a fast equilibrium between the *trans*-P—Fe—H isomer and the three *cis*-P—Fe—H isomers should represent the general situation. The vicinal CH protons are weakly coupled, indicating a dihedral angle of ca. 90°. Finally, a ^{57}Fe−^{31}P inverse-INEPT experiment allowed the determination of $^1J(^{31}P,^{57}Fe) = 65$ Hz (^{57}Fe ~2%).

5b reacts quantitatively with $KHFe(CO)_4$ to afford crystals of **7**, which are stable in the air.[15] From an X-ray diffraction study,[16] the hydride ligand is located at Fe−H = 1.57(6) Å and occupies an axial position of a distorted trigonal bipyramid, whereas the phosphorus atom lies in the equatorial plane (Figure 3). Such an "unexpected" *cis* geometry has been observed for $PPN^+[HFe(CO)_3\{P(OPh)_3\}]^-$, which is also exceptionally stable in the air.[17] A $Me_3N^+\cdots{}^-HFe$ contact occurs in the vicinity of the hydride; since ∠H(1)−C(103)−N(1) = 112.8°, the expected H(1)−C(103) contact distance should be roughly equal to $d_c = C{-}H + r_w(H) + r_w(H(1))$. Taking the average C−H bond length as 1.09 Å and the van der Waals radius of H as $r_w(H) = 1.11$ Å,[18] one obtains $d_c = 2.31$ Å, which accurately fits the measured value H(1)−C(103) = 2.310 Å. If this intramolecular pairing was retained in solution, it would favor the possibility of the "zwitterionic control" hypothesis for stereoselective hydride transfer (Figure 1). This is also supported by a strong ^{1}H−^{1}H NOE (ca. 36%) of NMe_3^+ on $^-$HFe, which has been measured in CD_3CN. For steric reasons, this electrostatic folding back would be highly unlikely in a *trans*-H−Fe−P isomer. The *cis* geometry is confirmed by the first-order analysis of the IR spectrum in THF.[15] The ^2J(H,P) constant increases with temperature (from 15.4 Hz at 233 K to 26.8 Hz at

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[10] NMR data for **3a** in $CDCl_3$: ^{31}P (81 MHz) δ (ppm) 131.3. Procedure and full spectroscopic data available in the Supporting Information.

[11] Procedure for **5b**: 1.15 g (5 mmol) of Ph_2PNMe_2 and 0.85 g (2.5 mmol) of **2b** are dissolved in 5 mL of refluxing acetonitrile. After 72 h, the reaction medium is cooled and the solvent is evaporated. The residue is triturated in 20 mL of ether over 3 h, during which time a white solid precipitates. The solid is filtered, washed with ether (2 × 20 mL), and then dissolved in 10 mL of CH_2Cl_2: the resulting solution is filtered and evaporated. **5b** (1.08 g) is obtained as a white hygroscopic solid (82% yield). NMR data for **5b** in $CDCl_3$: ^{31}P (81 MHz) δ (ppm) 113.0, −139.1 (sept, $^1J_{PF} = 710$ Hz); ^{1}H (200 MHz) δ (ppm) 1.37 (d, ^3J(H,H) = 7 Hz, 3H; CH_3), 2.92 (s, 9H; $(CH_3)_3$), 3.44 (q, ^3J(H,H) = 7 Hz, 1H; CHN), 5.45 (d, ^3J(H,P) = 7 Hz, 1H; CHO), 7.25 (5H; aromatic CH), 7.39−7.54 (10H; aromatic CH), the H_2O signal is also present; ^{13}C (50 MHz) δ (ppm) 7.83 (s; CH_3), 52.22 (s; $(CH_3)_3$), 75.35 (d, ^2J(C,P) = 6 Hz; CHO), 77.58 (s; CHN), 126.77 (s; ortho(PhC)), 128.77 (s; *para*(PhC)), 129.05 (s; *meta*(PhC)), 128.89, 129.33, 129.44, 130.05, 130.21, 130.56, 131.74, 132.60, and 132.99 (Ph_2P signals), 136.79 (s; ipso(PhC)), 138.88 (d, ^1J(C,P) = 20 Hz; ipso(PhP)), 139.21 (d, ^1J(C,P) = 23 Hz; ipso(PhP)).

[12] (a) Zhou, J.-Q.; Alper, H. *Organometallics* **1994**, *13*, 1586. (b) Cardaci, G. *J. Chem. Soc., Dalton Trans.* **1984**, 815. (c) Yang, K.; Bott, S. G.; Richmond, M. *Organometallics* **1994**, *13*, 3767.

[13] NMR data for **6** in DMSO-d_6: ^{31}P (162 MHz) δ (ppm) 220.6. Procedure and full spectroscopic data available in the Supporting Information.

[14] Ash, C. E.; Darensbourg, M. Y; Hall, M. B. *J. Am. Chem. Soc.* **1987**, *109*, 4173.

[15] Procedure for **7**: a solution of 0.208 g (1.0 mmol) of $KHFe(CO)_4$ in 2.5 mL of THF[2c] is added at 25 °C to a solution of 0.589 g (1.1 mmol) of **5b** in 2.5 mL of THF. After 3 h, 0.185 g of a KPF_6 precipitate is filtered (100%). A crystalline first crop of hygroscopic **7**·THF deposits from the THF supernatant. NMR data for **7** in DMSO-d_6: ^{31}P (162 MHz) δ (ppm) 191.9; ^{1}H (400 MHz) (δ, ppm) −9.06 (d, ^2J(P,H) = 25.0 Hz, 1H; FeH), 1.63 (d, ^3J(H,H) = 6.7 Hz, 3H; CH_3), 3.28 (s, 9H; $(CH_3)_3$), 3.77 (q, ^3J(H,H) = 6.7 Hz, 1H; CHN), 6.57 (d, ^3J(H,P) = 8.4 Hz, 1H; CHO), 7.1−7.2 (m, 5H; (C)), 7.19 (t, ^3J(H,H) ≈ 7 Hz, 2H; *meta*(B)), 7.23 (t, ^3J(H,H) ≈ 7 Hz, 1H; *para*(B)), 7.50 (t, ^3J(H,H) = 7.2 Hz, 1H; *para*(A)), 7.53 (dd, ^3J(H,P) ≈ 8 Hz, ^3J(H,H) = 7.2 Hz, 2H, *ortho*(B)), 7.57 (t, ^3J(H,H) = 7.2 Hz, 2H; *meta*(A)), 8.06 (dd, ^3J(H,P) = 8.2 Hz, ^3J(H,H) = 7.2 Hz, 2H; *ortho*(A)), signals of THF and H_2O are also present; ^{13}C (100 MHz) δ (ppm) 7.80 (s; CH_3), 51.14 (s; $(CH_3)_3$), 73.75 (d, ^2J(C,P) = 9.8 Hz; CHO), 75.25 (d, ^2J(C,P) = 7.5 Hz; CHN), 126.85 (d, ^3J(C,P) = 9.3 Hz; *meta*(B)), 127.10 (s; *ortho*(C)), 127.18 (s; *para*(C)), 127.55 (s; *meta*(C)), 127.74 (d, ^3J(C,P) = 9.1 Hz; *meta*(A)), 128.67 (s; *para*(B)), 128.85 (s; *para*(A)), 130.35 (d, ^2J(C,P) = 13.4 Hz; *ortho*(A)), 131.27 (d, ^2J(C,P) = 14.3 Hz; *ortho*(B)), 139.08 (s; *ipso*(C)), 144.83 (d, ^1J(C,P) = 33.2 Hz; *ipso*(B)), 145.53 (d, ^1J(C,P) = 46.1 Hz; *ipso*(A)), 222.79 ppm (d, ^2J(C,P) = 4.5 Hz; ^2J(C,H) = 12.5 Hz; C≡O). IR (THF): ν (cm^{-1}) 1946 (m; C≡O, A'_1 band), 1889 (w; Fe−H), 1853 (s; C≡O A'' band), 1832 (m; C≡O, A'_2 band).

[16] Crystal structure analysis of **7**: $C_{27}H_{30}NO_4PFe{\cdot}C_4H_8O$, M = 587, triclinic, $a = 9.667$ Å, $b = 9.547$ Å, $c = 10.179$ Å, $\alpha = 94.44°$, $\beta = 110.03°$, $\gamma = 117.93°$, space group $P1$, $Z = 1$, μ(Mo Kα) = 59.3 mm^{-1}, $\rho_{calcd} = 1.302$ Mg m^{-3}, 2622 measured reflections, 2388 observed reflections ($I > 3\sigma(I)$), 357 parameters refined, $R = 0.0384$ ($R_w = 0.0315$). The reflections were measured on a ENRAF-Nonius CAD4 diffractometer with Mo Kα radiation ($\lambda = 0.710\,73$ Å) by using the $\omega/2\theta$ scan method. Three reference reflections were monitored periodically. The structure was solved by direct methods (SHELXS86: Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509) and refined in accord with the crystal program package. The positions of all hydrogen atoms were determined from difference Fourier maps but introduced in calculated positions (C−H = 0.98 Å) and recalculated after each cycle of refinement. The hydride H(1) has been placed by using a hydride location program (XHYDEX). This position was provided by difference Fourier syntheses and refined with a isotropic thermal parameter fixed at $U_{eq} = 0.08$ Å^2. All non-hydrogen atoms were anisotropically refined. Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ, U.K., on quoting the full journal citation.

[17] Ash, C. E.; Kim, C. M.; Darensbourg, M. Y.; Rheingold, A. M. *Inorg. Chem.* **1987**, *26*, 1357. In contrast, $Et_4N^+[HFe(CO)_3\{PPh_3\}]^-$ is reported to be preferentially *trans*: Ash, C. E.; Delord, T.; Simmons, D.; Darensbourg, M. Y. *Organometallics* **1986**, *5*, 17.

[18] Chauvin, R. *J. Phys. Chem.* **1992**, *96*, 9194.

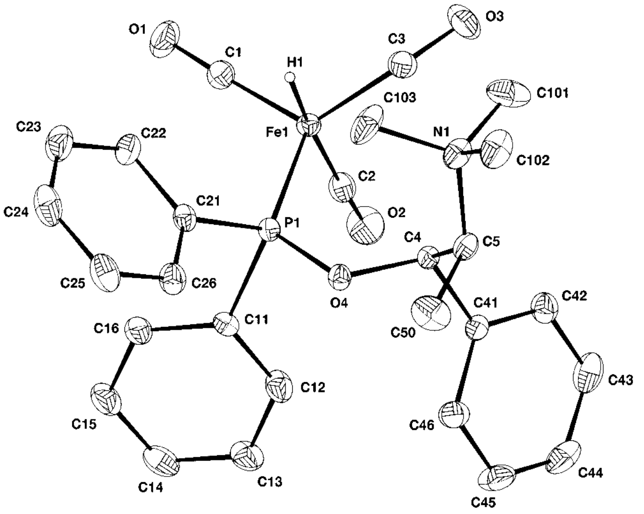

Figure 3. X-ray crystallographic structure of **7**. Selected bond lengths (Å) and angles (deg): Fe(1)−P(1) = 2.159(1); Fe(1)−C(1) = 1.731(5); Fe(1)−C(2) = 1.749(5); Fe(1)−C(3) = 1.742(5); Fe(1)−C(103) = 4.338; Fe(1)−H(1) = 1.57(6); P(1)−O(4) = 1.681(3); H(1)−C(103) = 3.310; Fe(1)−P(1)−O(4) = 120.5(1); P(1)−Fe(1)−C(2) = 96.8; P(1)−Fe(1)−H(1) = 86.4(20); C(1)−Fe(1)−C(2) = 99.9(2); C(1)−Fe(1)−C(3) = 116.6(2); C(2)−Fe(1)−C(3) = 94.2(2); C(1)−Fe(1)−H(1) = 79.3(20); C(2)−Fe(1)−H(1) = 176.8(21); C(3)−Fe(1)−H(1) = 83.5(21); C(11)−P(1)−C(21) = 98.3(2); H(1)−C(103)−N(1) = 112.8; O(4)−C(4)−C(5)−N(1) = −87.28.

303 K and 31.7 Hz at 343 K in CD_3CN) (Figure 4) and depends on the solvent (in DMSO-d_6,[15] from 25.0 Hz at 303 K to 33.6 Hz at 373 K). This rather rare phenomenon has been previously observed in nonzwitterionic hydridotricarbonylferrates only for *trans*-H−Fe−P arrangements. However, the unprecedented chelation in **7** is likely to perturb the temperature dependence of the H−Fe−P angle and, therefore, that of the ^2J(H,P) coupling constant. At 303 K, the three carbonyl carbons are equivalent on the ^{13}C NMR time scale, as reported for $PPN^+[cis\text{-}HFe(CO)_3\{P(OPh)_3\}]^-$:[17] this suggests a fast exchange of the carbonyl ligands of the distorted TBP via a pseudorotation process. In such a process, the hydrogen and the phosphorus ligands would not be independent, due to the chelating situation which would retain them in a *cis* position. In conclusion, a general, fast equilibrium between the three possible *cis* isomers would explain our spectroscopic observations. A difference between the relative weights of these isomers in **6** and **7** (due to a difference of the steric requirements of the phenyl and dimethylamino substituents at the P atom) could account for the difference in the order of magnitude and the temperature dependence of ^2J(P,H).

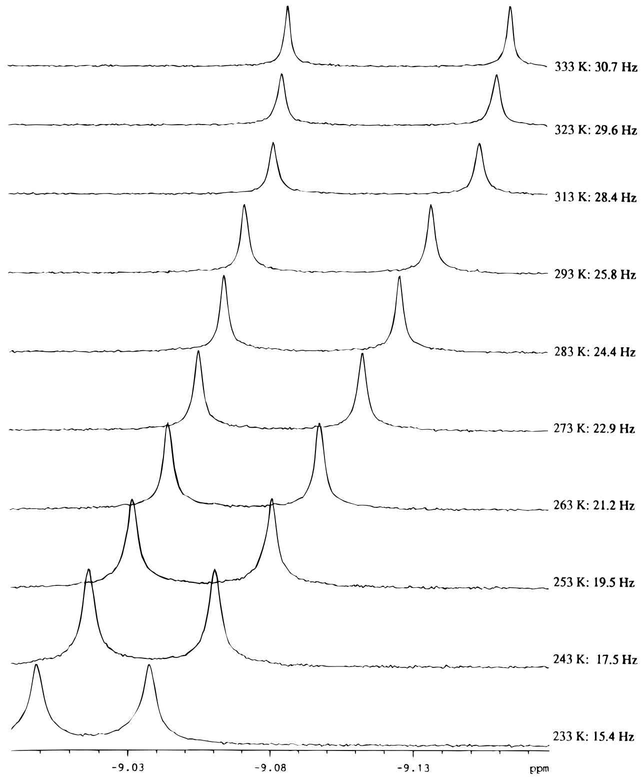

Figure 4. Variation of the ^2J(P,H) coupling constant of **7** with temperature in ^1H NMR (CD_3CN).

$^1H-^1H$ GE-COSY-DQF correlations show that ^1H resonances of each phenyl ring are well-separated. All signals of one PhP ring are deshielded (appearing in the region A, 8−7.5 ppm) with respect to signals due to the other PhP ring (appearing in region B, 7.5−7 ppm), whereas all signals of the PhC ring occur in the region C (6.9−7.2 ppm). This observation supports the occurrence of a face-to-edge conformation of the Ph_2P group, the B ring lying in the shielding cone of the A ring and the rotation of the P−Ph bonds being restricted to a 180° flip-flop. Finally, all ^{13}C signals were assigned using ^1J and long-range $^1H-^{13}C$ GE-HMQC experiments; the vicinal CH protons are weakly coupled (indicating a dihedral angle close to 90°), and a $^{57}Fe-^{31}P$ inverse-INEPT experiment gives $^1J(^{31}P,^{57}Fe) \approx 60$ Hz.

The reactivity of these chiral zwitterionic complexes is currently being investigated. The family of ephosium ligands can be naturally extended to other chiral amino alcohols and other substituents quaternizing the nitrogen atom. Although the phosphinite function is easily and stereospecifically introduced, the corresponding less labile phosphine ligands could also be envisioned. Besides the zwitterionic strategy, cationic or polycationic complexes involving ephosium-type ligands might act as asymmetric catalysts in aqueous or biphasic media.

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Supporting Information Available: Tables giving atomic coordinates, thermal parameters, and bond distances and angles, the abstract form for the Cambridge Crystallographic Database for **7**, and text giving procedures and spectroscopic data for **2a**, **3a**, **4a**, and **6** (6 pages). Ordering information is given on any current masthead page.

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