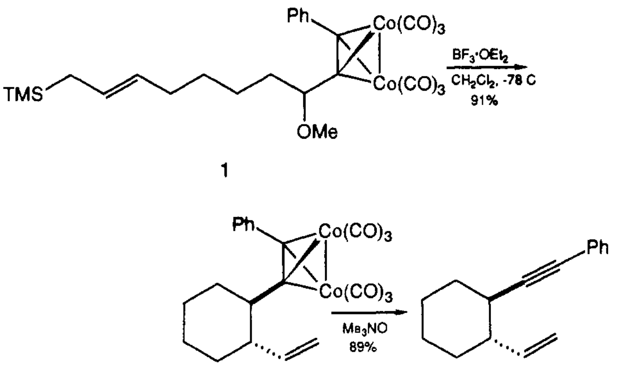
is shown could be formed preferentially by selective cobalt participation in the Lewis acid assisted heterolysis of the methoxyl or through nonselective cobalt participation and a subsequent suprafacial migration of the ethylidene group (resulting in syn–anti isomerization).[8] A transition state with a synclinal alignment of the two Π systems and with the methyl groups antiperiplanar to the Π systems (relative face selection = *lk*) will result in the syn-alkylated (*l*) products that are observed to predominate (Si–Si alignment is illustrated).[9] The model serves to rationalize the aforementioned features of this reaction, including the role of the substituent attached to the acetylene–cobalt complex. The larger substituent would serve to increase the value of $\Delta\Delta G^{\ddagger}$ for diastereomeric transition states leading to syn and anti alkylated products. If the anti product were obtained through the related synclinal transition state (Re–Si alignment in Figure 1), van der Waals strain would result from the interaction of the methyl group on the enol ether with the substituent (R) on the cobalt acetylene complex.

The exocyclic internal alkylation of the allylic silane **1** (eq 6)



conforms to the same transition-state model. In this reaction the six-membered ring **2** is formed with complete stereocontrol (trans) with respect to the two appendages on the newly formed ring. Oxidative decomplexation of the extraannular cobalt complex provided acetylene **3**.

Endocyclic internal alkylation to provide intraannular cobalt complexes of cycloalkynes has also been achieved and in combination with the Pauson–Khand cyclization provides polycycles of interest to natural and unnatural products synthesis. Examples of this process that afford six-, seven-, and eight-membered products are illustrated in Scheme I (eq 7–10). Complexation of the precursor acetylene with dicobalt octacarbonyl in each of these examples results in a substantial change in bond angles at the sp carbon centers. The intermediate can be viewed as a cis-allyl cation equivalent with a regiochemical imperative for reaction at its terminus. Oxidative removal of the cycloacetylenic ligand with Me_3NO does not lead to the cycloalkyne product. This reaction proceeds along alternative paths that have not been fully elucidated. The intraannular cobalt complexes are excellent participants in the Pauson–Khand cyclization reaction. For example, cyclooctyne **5** gave rise to a 1:1 mixture of cyclopentenones **6a** and **6b** in 67% yield on treatment with norbornene and 1 atm of carbon monoxide in refluxing benzene (eq 7).[10]

In order to eliminate the formation of unwanted isomers in the second cyclization process, the internal Nicholas reaction can be coupled to a subsequent internal Pauson–Khand reaction as depicted in eq 10. The allyloxy acetal **11** reacts more slugglishly than the corresponding ether but proceeds at room temperature (10 min) to afford a 5:1 mixture of **12** and the cis isomer in 75% yield.[11,12] Treatment of **12** with 1 atm of carbon monoxide in benzene at 60 °C for 4 h provided a single tricyclic material **13** in 85% yield. The assignment of stereochemistry follows from ^1H NMR experiments (NOE difference, *J* value measurements). Comparison of structure **13** with epoxydictymene **14**,[13] a representative member of the fusicoccin class of diterpenes, suggests this reaction sequence may prove to be of value in the synthesis of members of this class of compounds.

Acknowledgment. This investigation was supported by the NSF (Presidential Young Investigator Award), Dreyfus Foundation (Dreyfus Teacher–Scholar Grant), A.P. Sloan Foundation, and Pfizer, Inc., to whom we are grateful. Fellowship support (for T.S.) was contributed by the Berlex Laboratories in the form of a Berlex Predoctoral Fellowship. A Dox Fellowship (for W.E.C.) is gratefully acknowledged.

Supplementary Material Available: Experimental procedures as well as NMR, IR, and mass spectral data for the compounds studied (11 pages). Ordering information is given on any current masthead page.

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(7) Evidence in support of the cannonical structure with charge localized on cobalt is found in the increase in the carbonyl stretching frequency in the cationic complexes (Connor, R. G.; Nicholas, K. M. *J. Organomet. Chem.* **1977**, *125*, C45) and by analogy with the isolobal tricobalt alkylidyne cluster compounds (Ediden, R. T.; Norton, J. R.; Mislow, K. *Organometallics* **1982**, *1*, 561).

(8) NMR studies implicate a significant barrier to rotation about the C–C+R_2 bond and to suprafacial migration of the ethylidene group: Padmonbahan, S; Nicholas, K. M. *J. Organomet. Chem.* **1983**, *268*, C23.

(9) Compare to: (a) Seebach, D.; Golinski, J. *Helv. Chim. Acta* **1981**, *64*, 1413. (b) Denmark, S.; Weber, E. J. *Helv. Chim. Acta* **1983**, *66*, 1655. (c) Denmark, S. E.; Weber, E. J. *J. Am. Chem. Soc.* **1984**, *106*, 7970. (d) Heathcock, C. H.; Norman, M. H.; Uehling, D. E. *J. Am. Chem. Soc.* **1985**, *107*, 2794. (e) Faller, J. W.; Lambert, C. *Tetrahedron* **1985**, *41*, 5755.

(10) Khand, I. U.; Pauson, P. L. *J. Chem. Soc., Perkin Trans. 1* **1976**, 30. Although it is likely that **6a** and **6b** exist as a mixture of stereoisomers (at the carbon bearing the vinyl group), we were not able to confirm this point.

(11) These two compounds were separated by SiO_2 chromatography. The major trans isomer was employed in the subsequent cyclization reaction.

(12) (a) Cockerill, G. S.; Kocienski, P.; Treadgold, R. *J. Chem. Soc., Perkin Trans. 1* **1985**, 2093, 2101. (b) Majetich, G.; Hull, K.; Defauru, J.; Shawe *Tetrahedron Lett.* **1985**, *26*, 2755.

(13) Enoki, N.; Furusaki, A.; Suehiro, K.; Ishida, R.; Matsumoto, T. *Tetrahedron Lett.* **1983**, *24*, 4341.

Electrochemical and ESR Characterization of the Redox Behavior of Bis[tris(trimethylsilyl)methyl]diphosphene, $(Me_3Si)_3C—P{=}P—C(SiMe_3)_3$ (TsiP=PTsi)

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An explosive growth of interest and activity in the area of synthesis and characterization of diphosphenes followed the 1981' report of Yoshifuji and co-workers[1] on the synthesis of the first stable compound featuring a phosphorus–phosphorus $3p(\pi)$–$3p(\pi)$ double bond. Since then, some symmetrically as well as unsymmetrically substituted diphosphenes and diarsenes have been

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† Université de Provence.

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(1) Yoshifuji, M.; Shima, I.; Inamoto, N. J.; Hirota, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587. Bertrand, G.; Couret, C.; Escudié, J.; Majid, S.; Majoral, J. P. *Tetrahedron Lett.* **1982**, *23*, 3567. Couret, C.; Escudié, J.; Satgé, J. *Tetrahedron Lett.* **1982**, *23*, 4941. Cowley, A. H.; Kilduff, J. E.; Newman, T. J.; Pakulski, M. *J. Am. Chem. Soc.* **1982**, *104*, 5820. Review: Cowley, A. H. *Polyhedron* **1984**, *3*, 389.

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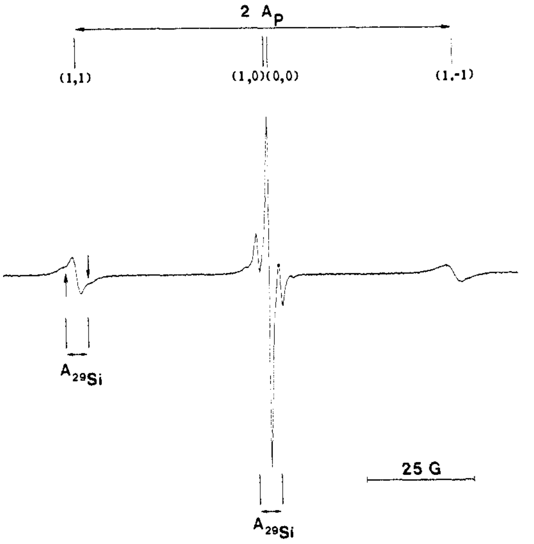

Figure 1. ESR spectrum of the bis[tris(trimethylsilyl)methyl]diphosphene anion radical electrogenerated in 1,2-dimethoxyethane with 0.1 M $(C_4H_9)_4NPF_6$ at 298 K.

prepared[2] and chemically and spectroscopically investigated by several groups.

We report in this paper the electrochemical and ESR characterization of the redox behavior of the di-trisyldiphosphene (TsiP═PTsi,(**1**) (Tsi = tris(trimethylsilyl)methyl or trisyl).

The redox behavior of **1** was investigated by cyclic voltammetry and pulse voltammetry at a platinum or a mercury-coated platinum electrode, using [n-$Bu_4N\,PF_6$] as the supporting electrolyte in 1,2-dimethoxyethane (DME) or acetonitrile (ACN).

Oxidation of **1** at a platinum electrode in ACN occurred at E_p(ox) = 1.14 V vs. SCE. The oxidation wave was irreversible even at a fast potential sweep rate (2 V/s) and no cation radical was detected even when the oxidation was performed within the cavity of an ESR spectrometer.

The diphosphene **1** showed a rapid reversible one-electron reduction at a mercury-coated platinum electrode; E_p(red)= −1.73 V vs. SCE. When the electroreduction of **1** was performed in the cavity of an ESR spectrometer, the persistent spectrum (g = 2.0111) shown in Figure 1 was observed.[3] Addition of sodium naphthalide in THF to a solution of TsiP═PTsi gave the same ESR spectrum. We assign this spectrum to the anion radical $(TsiP{=}PTsi)^{-\cdot}$, $\mathbf{1}^{-\cdot}$.[4]

The unusual aspect of the ESR spectrum of $\mathbf{1}^{-\cdot}$ deserves comment. The second-order coupling to two equivalent phosphorus nuclei is expected to give a four-line spectrum, since the first-order degeneracy between the (0,0) and the (1,0) transitions is removed[5] (Figure 1). The separation between the two outer lines is equal to $2A_P$ and thus A_P = 43.5 G. The separation between the two inner lines is given by $(A_P)^2/B$ = 0.6 G, (B is the magnetic flux density corresponding to the (1,0) transition) and was too small to permit resolution of the lines corresponding to the (1,0) and (0,0) transitions (Figure 1).

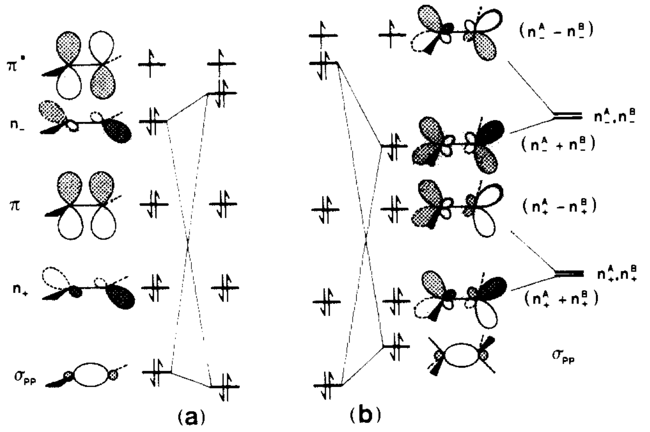

Figure 2. Schematic drawing of the highest MO of the anion radical $[TsiP{=}PTsi]^{-\cdot}$ (a) assuming a π configuration and (b) assuming a σ configuration.

On the other hand, the β-coupling with the ^{29}Si nucleus was clearly resolved for the (0,0) transition, $A(^{29}Si)$ = 5 G, and appeared as shoulders in the case of the (1,1) transition. The different lines of the ESR spectrum of $\mathbf{1}^{-\cdot}$ exhibited very different line widths. The same kinds of ESR spectra, showing the same line-width broadening, were observed for a series of phosphine dimer cation radicals $(X_3PPX_3)^{+\cdot}$[6] and a series of tetraaryl diphosphine cation radicals $(Ar_2PPAr_2)^{+\cdot}$.[7] However, for these ion radicals, the phosphorus splitting was very large, and the inner lines corresponding to the (1,0) and (0,0) transitions were very well resolved.

In the case of the tetraaryl diphosphine cation radicals, the line-width broadening was interpreted in terms of the nuclear spin relaxation induced by the time-dependent anisotropic dipolar phosphorus interaction.[7] The same model can be satisfactorily applied to the radical $\mathbf{1}^{-\cdot}$. The small phosphorus splitting observed for the radical $\mathbf{1}^{-\cdot}$ suggests that the phosphorus centers in $\mathbf{1}^{-\cdot}$ have a π configuration.[8] The P_{3s}-orbital population for the semioccupied MO, derived from the A_P value, is only 2.4%. This small value is very similar to those found for the phosphinyl radicals $Y_2P\cdot$[9] for which a π configuration has been established.

We have recently shown by ESR that the tetraaryl-diphosphine cation radicals $(Ar_2PAr_2)^{+\cdot}$ have a σ configuration and are significantly bent at the phosphorus centers.[7] The same conclusion was reached[10] independently by ab initio calculations for the diphosphine cation radical $(H_2PPH_2)^{+\cdot}$. This pyramidal geometry precludes any three-electron π stabilization, and, as suggested by T. Clark,[10] these cations are strongly stabilized by strong mixing between the high-lying unsymmetrical lone pair combinations (n_-) and the phosphorus–phosphorus σ-bonding orbital σ_{PP}.

It is worth to discuss qualitatively the preference of radical anion $\mathbf{1}^{-\cdot}$ for a π configuration. A schematic drawing of the highest-occupied molecular orbitals (MO) corresponding to the π configuration and the σ configuration of trans $(HP{=}PH)^{-\cdot}$ is shown in Figure 2.

For a π configuration, which was shown to be the preferred configuration by EHT calculations, the different MO's (Figure 2a) have the same characteristic as those calculated[11] for the

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(3) (a) A 1,2-dimethoxyethane solution of bis[tris(trimethylsilyl)methyl]diarsene, TsiAs═AsTsi,[3b] showed a rapid reversible one-electron reduction at a mercury-coated platinum electrode; E_p(red) = −1.82 V vs. SCE. When the electroreduction was performed at room temperature in the cavity of an ESR spectrometer, a persistent broad signal was observed. Unfortunately, no coupling was clearly resolvable in the temperature range −80 to +30 °C. The lack of resolvable hyperfine structure is probably due to quadrupole relaxation of the ^{75}As nuclear spin.[3c] (b) Couret, C.; Escudié, J.; Madaule, Y.; Ranaivonjatovo, H.; Wolf, J. G. *Tetrahedron Lett.* **1983**, 2769. (c) Gynane, M. J. S.; Hudson, A.; Lappert, M. F.; Power, P. P.; Goldwhite, H. *J. Chem. Soc., Dalton Trans.* **1980**, 2428.

(4) The sodium naphthalide reduction of ArP═PAr (Ar = 2,4,6-tri-*tert*-butylphenyl) was reported to give an ESR signal with A_p = 55 G and g = 2.010, which was assigned to the anion radical $[ArP{=}PAr]^{-\cdot}$. Cetinkaya, B.; Hudson, A.; Lappert, M. F.; Goldwhite, H. *J. Chem. Soc., Chem. Commun.* **1982**, 609. Cetinkaya, B.; Hitchcock, P. B.; Lappert, M. F.; Thorne, A. J.; Goldwhite, H. *J. Chem. Soc., Chem. Commun.* **1982**, 691.

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(6) Gara, W. B.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1978**, 150.

(7) Culcasi, M.; Gronchi, G.; Tordo, P. *J. Am. Chem. Soc.* **1985**, *107*, 7191.

(8) A free radical has a π configuration if the contributions of the ns orbitals to its SOMO is negligible.

(9) Griller, D.; Roberts, B. P.; Davies, A. G.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 554. Roberts, B. P.; Singh, K. *J. Organomet. Chem.* **1978**, *159*, 31. Gynane, M. J. S.; Hudson, A.; Lappert, M. F.; Power, P. P.; Goldwhite, H. *J. Chem. Soc., Dalton Trans.* **1980**, 2428.

(10) Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1985**, *107*, 2596. Clark, T. *J. Am. Chem. Soc.* **1985**, *107*, 2597.

neutral trans diphosphene HP=PH. For the σ configuration (Figure 2b) the highest MO's are the σ_{PP} and the orbitals obtained by the mixing of the two symmetrical (n^A_+, n^B_+) or the two unsymmetrical (n^A_-, n^B_-) phosphorus "lone-pair" combinations.

For the two configurations, the SOMO (Figure 2) is not of the right symmetry to mix with the subjacent filled MO. However, as in the case of the diphosphine cation radical, a strong interaction is expected to occur between the n_- orbital (π configuration) or the $(n^A_- + n^B_-)$ orbital (σ configuration) and the σ_{PP}. In the two cases the interaction involves two filled orbitals and thus is expected to destabilize the system, while it was stabilizing in the case of $(H_2PPH_2)^{+\cdot}$. However, since the two orbitals involved in the interaction have a lower energy gap and a better overlap for the σ configuration than for the π configuration, the destabilizing effect is stronger for the former and is expected to favor the π configuration.

Finally, it may be noted in passing that the anion radicals $(TsiP{=}PTsi)^{-\cdot}$ and[4] $(ArP{=}PAr)^{-\cdot}$ are the first reported molecules for which the electronic structure involves a three-electron P–P π-bond.

Acknowledgment. We thank the Centre National de la Recherche Scientifique and the LETI (CEA Grenoble) for financial support, Pr. Y. Ayant, and Dr. N. Kernevez for helpful discussions, and Pr. T. Clark who communicated to us the results of his preliminary ab initio calculations on $(HP{=}PH)^{-\cdot}$ and $(H_2P{=}P)^{-\cdot}$.

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(11) Lee, J. G.; Cowley, A. H.; Boggs, J. G. *Inorg. Chim. Acta* **1983**, *77*, L61–L62.

Novel Technique for the Generation of Bis(polyfluoroalkyl) and Polyfluoroalkyl Nitroalkyl Nitroxides. ESR Verification of Mechanistic Propositions for the Reactions between Polyfluorodiacyl Peroxides and Carbanions Derived from Secondary Nitroalkanes[†]

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Received September 6, 1985

Polyfluoroalkyl akyl nitroxide radicals have been investigated by Klabunde,[1] Konaka and Terabe,[2] Tabata and co-workers,[3] Kochi,[4] and others. Rather surpisingly, only one nitroxide of the bis(perfluoroalkyl) type, i.e., bis(trifluoromethyl) nitroxide, has been studied in detail.[5-7] Now, we wish to communicate a novel and general method for the generation of bis(polyfluoroalkyl) nitroxides **9** as well as polyfluoroalkyl nitroalkyl nitroxides **10** by making use of the spontaneous electron-transfer-initiated reactions between polyfluorodiacyl peroxides **1** and carbanions derived from nitroalkanes **2**. Product studies of these novel reactions accord with a mechanism which reckons in an initial electron transfer from the carbanion **2** to the peroxide **1** (cf. Scheme I).[8] It also speculates that one of the major products, an aldehyde or ketone **6**, comes from the fragmentation of an unstable intermediate, **5**. Another key unstable intermediate is believed to be the acyl nitrite **7**. Decarboxylation of **7** should lead directly to the in situ for-

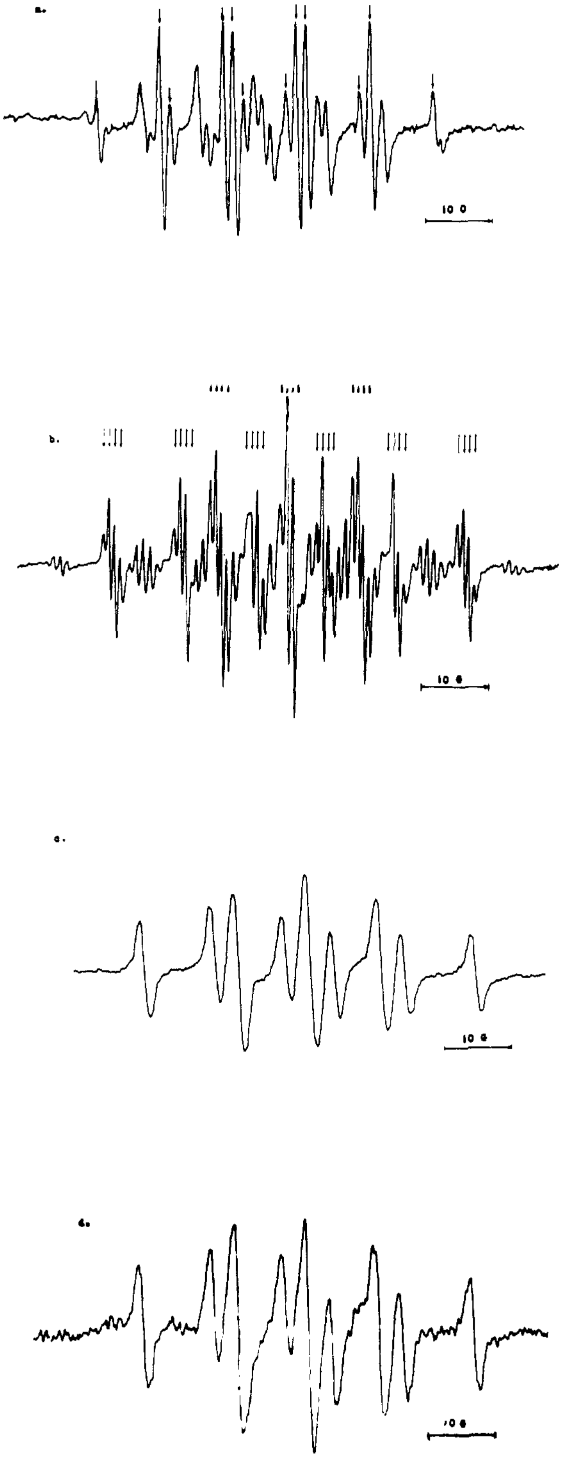

Figure 1. Some representative ESR spectra of nitroxides **9** and **10** obtained in $CClF_2CCl_2F$ at 20 °C. (a) mixture of $CF_3N(O)CF_3$ (**9a**) and $CF_3N(O)CMe_2NO_2$ (**10a**, represented by ↓), from **1a** + **2a**; (b) mixture of $C_2F_5N(O)C_2F_5$ (**9b**) and $C_2F_5N(O)CMe_2NO_2$ (**10b**, ↓), from **1b** + **2a**; (c) n-$C_7F_{15}N(O)CMe_2NO_2$ (**10d**) from **1d** + **2a**; (d) **10d** from **1d** + 2-nitroso-2-nitropropane + Cu^0.

[†] Dedicated to Professor Cheves Walling on the occasion of his 70th birthday.

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(7) Chatgilialoglu, C.; Walastesta, V.; Ingold, K. U. *J. Phys. Chem.* **1980**, *84*, 3597.

(8) Zhao, C.-X.; Qu, Y.-L.; Jiang, X.-K.; Jin, X.-M. *Acta Chim. Sin.* **1985**, *43*, 1184.