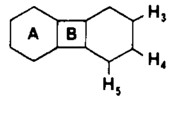
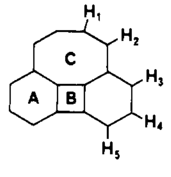
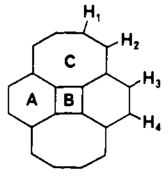
Table I. Ring Currents[a] and ^{1}H NMR Chemical Shifts[b] for Hydrocarbons 7, 8, and 6



7



8



6

	compd 7	compd 8	compd 6
	Calculated Ring Current		
ring			
A	+0.608	+0.369	-0.091
B	-0.804	-0.745	-1.164
C		-0.706	-1.071
proton	Observed Chemical Shift		
1		4.61	3.63[c]
2		4.74	3.59[c]
3	6.73	5.83	4.55
4	6.73	6.21	4.55
5	6.62	6.05	

[a] Benzene = +1.00. This work; see ref 13a. [b] In ppm downfield from Me_4Si. 300-MHz spectra taken in $CDCl_3$, Me_4Si internal reference. Multiplets analyzed by LAOCOON III (ref 10). [c] Assignments given here assume a slightly paratropic ring current for A ring of 6. For an explanation of possible ambiguity, see ref 13b,c,d.

benzenoid protons in **6** show an upfield shift of 2.41 ppm relative to **5**, while the α and β cycloocta protons are shifted upfield by 3.15 and 1.73 ppm, respectively. The observed magnetotropism for this and similar compounds[11] appears to be well described by an iterative Hückel-McWeeny ring current model[12-14] (see Table I).

It is worthwhile to consider the qualitative origin of benzenoid atropism in **6**. In addition to three rings of [4*n*] type, compound **6** has a coronoid topology with a central ring of $[4]\pi$ and a periphery of $[16]\pi$. While the importance of peripheral circuits has been shown for some systems,[8,15] the perturbation by the central substructure may be so great as to remove any simple predictive capability based solely upon the periphery.[16] Such peripheral analyses are, to some degree, implicit in the consideration of all conjugated circuits, as in the approaches of Randić[17] and Gomes.[18] According to these methods, benzenoid atropism in **6** arises from the net cancellation of numerous Hückel and anti-Hückel conjugated circuits, as opposed to the situation encountered in the Clar-Robinson "nonsextet" rings of polycyclic aromatics,[19] wherein reduced diatropism results from the virtual or complete absence of conjugated circuits involving the affected ring.[17b]

Registry No. 1, 63548-78-7; **2**, 87729-44-0; **3**, 87739-06-8; **4**, 87729-45-1; **5**, 87729-46-2; **6**, 64074-44-8; **7**, 259-79-0; **8**, 36230-20-3.

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[11] (a) Wilcox, C. F., Jr.; Uetrecht, J. P.; Grohman, K. K. *J. Am. Chem. Soc.* **1972**, *94*, 2532. (b) Wilcox, C. F., Jr.; Uetrecht, J. P.; Grantham, G. D.; Grohmann, K. G. *Ibid.* **1975**, *97*, 1914-1920.

[12] McWeeny, R. *Mol. Phys.* **1958**, *1*, 311.

[13] (a) Ring currents were calculated by a self-consistent HMO technique used previously (ref llb). For an excellent discussion of ring currents in paratropic systems, see the following references. (b) Coulson, C. A.; Mallion, R. B. *J. Am. Chem. Soc.* **1976**, *98*, 592-598. (c) Gomes, J. A. N. F.; Mallion, R. B. *J. Org. Chem.* **1981**, *46*, 719-727. (d) Mallion, R. B. *Pure Appl. Chem.* **1980**, *52*, 1541-1548.

[14] Several more highly fused derivatives of **6** and **8** have now been prepared, and the observed proton chemical shifts correlated with ring current calculations. Complete synthetic, spectroscopic, and theoretical details will be presented in a full paper.

[15] (a) Platt, J. R. *J. Chem. Phys.* **1954**, *22*, 1448-1458. (b) Müllen, K. *Helv. Chim. Acta* **1978**, *61*, 2307. (c) Minsky, A.; Meyer, A. Y.; Hafner, K.; Rabinovitz, M. *J. Am. Chem. Soc.* **1983**, *105*, 3975-3981.

[16] This point is particularly evident in the case of cycloocta[*def*]biphenylene **8**.

[17] (a) Randić, M. *J. Am. Chem. Soc.* **1977**, *99*, 444-450; (b) *Pure Appl. Chem.* **1980**, *52*, 1587-1596.

[18] Gomes, J. A. N. F. *Theor. Chim. Acta* **1981**, *59*, 333-356.

[19] (a) Clar, E. "The Aromatic Sextet"; Wiley: London and New York, 1972. (b) Clar, E. "Polycyclic Hydrocarbons"; Academic Press: London and New York; Springer-Verlag: Berlin, 1964; Vol. 1.

A β-Metal Ketone Strategy. Reactions of Siloxycyclopropanes with Silver(I) Tetrafluoroborate and Copper(II) Tetrafluoroborate Leading to 1,6-Diketones

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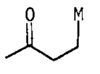
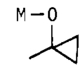
Received July 6, 1983

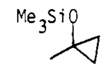
Development of new synthetic methodology for bond connection β to carbonyls constitutes one of the main challenging themes in modern organic synthesis.[1] For this purpose the use of β-metal-substituted ketones **1** would be most straightforward. However,



1



2



3

the reported result of the reaction of **1** where the metal M is an alkali metal seems discouraging because of the inevitable isomerization of **1** to more stable form **2** by internal nucleophilic addition.[2,3] For the efficient carbon-carbon bond formation β to carbonyls the use of other elements such as transition metals for M in **1** seems attractive, although in general they are hardly accessible.[4,5]

Our strategy for **1** is that electrophilic ring opening of siloxycyclopropane **3** by naked (or ligand free) transition-metal ions will give β-transition-metal ketone **1** efficiently with elimination of a trialkylsilyl moiety.[6] Thus, the reactions of siloxycyclopropane **3** with silver(I) tetrafluoroborate, $AgBF_4$, and copper(II) tetrafluoroborate, $Cu(BF_4)_2$, have been studied. We wish to report here the new carbon-carbon bond-forming reaction in which the intervension of β-silver- or β-copper-substituted ketone as intermediates is suggested.

1-(Trimethylsiloxy)bicyclo[4.1.0]heptane(**4**) (5 mmol)[7] was added to the suspension of silver tetrafluoroborate ($AgBF_4$, 6 mmol) in anhydrous ether at -20 °C, under atmosphere of nitrogen. Over a period of 15 min the temperature was raised to 15 °C, while a silver mirror gradually appeared on the wall of the reaction vessel. After another 15 min, workup (aqueous NH_4Cl and aqueous $NaHCO_3$) and purification upon column

---

[1] Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 239.

[2] Hamon, D. P. G.; Sinclair, R. W. *J. Chem. Soc., Chem. Commun.* **1968**, 890.

[3] A review for synthetic equivalent of β-lithio ketones; see: Werstiuk, N. H. *Tetrahedron* **1983**, *35*, 205.

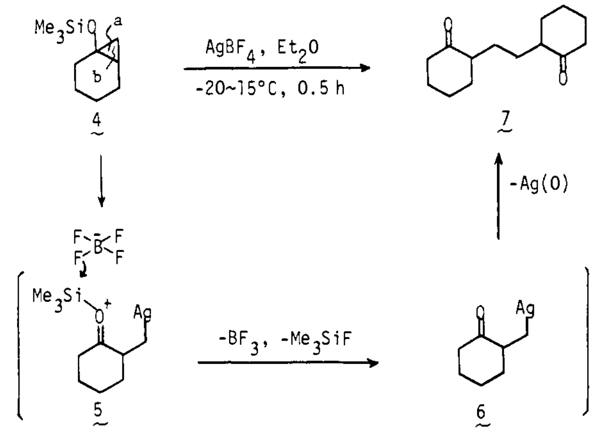
[4] Stable β-transition-metal ketones **1**; see for (a) M = Hg: DePuy, C. H.; Lanen, J. U. *J. Org. Chem.* **1974**, *39*, 3360. (b) M = Pt: Green, M.; Howard, J. A. K.; Mitrprachachon, P,; Pffefer, M.; Spencer, J. L.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc. Dalton Trans.* **1979**, 306. (c) M = Co: Wakatsuki, Y.; Aoki, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1974**, *96*, 5284. (d) M = Mn: Bennet, W. A.; Robertson, G. B.; Watt, R.; Whimp, P. O. *J. Chm. Soc., Chem. Commun.* **1971**, 752. (e) M = Fe: Jensen, J. E.; Campbell, L. L.; Nakanishi, S.; Flood, T. C. *J. Organomet. Chem.* **1983**, *244*, 61.

[5] Recently, Kuwajima and Nakamura have reported the aldol condensation via and isolation of β-titano esters; see: Nakamura, E; Kuwajima, I. *J. Am. Chem. Soc.* **1983**, *105*, 651; **1977**, *99*, 7360.

[6] Synthesis of β-mercuri ketones from siloxycyclopropanes and some transformations from them via transmetalation; see: Ryu, I.; Matsumoto, K.; Ando, M.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1980**, *21*, 4283.

[7] (a) Murai, S.; Aya, T.; Sonoda, N. *J. Org. Chem.* **1973**, *38*, 4354. (b) Ryu, I.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1977**, 4611. (c) Girard, C.; Conia, J. M. *J. Chem. Res. Synop.* **1978**, 182.

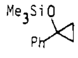
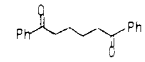
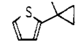
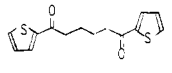
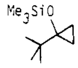
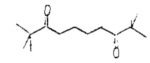
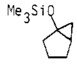
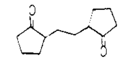
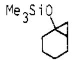
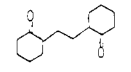
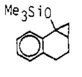
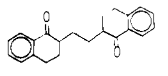
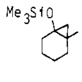
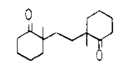
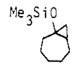
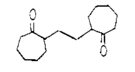
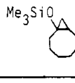
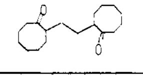
Scheme I



chromatography (SiO_2/*n*-hexane–Et_2O) afforded a 1,6-diketone, 1,2-dicyclohexan-2-on-1-ylethane (**7**) (70% GLC yield).[8]

The desilylative dimerization of the siloxycyclopropane **4** to the 1,6-diketone **7** occurred with site-selective cleavage of the cyclopropane ring at the bond a shown in Scheme I, and no product arising from bond b scission was obtained.[9] This dimerization β to carbonyls may be well accounted for by the intervension of β-silver ketone intermediate **6** (Scheme I). The electrophilic attack of Ag^+ at the least sterically crowded site of **4** followed by elimination of $(CH_3)_3SiF$[10] via **5** would give **6** which then would undergo dimerization to afford **7**.[11] The well-documented fact that primary alkyl silver(I) dimerizes to bis(alkane) is consistent with above postulation.[12] Electrophilic ring opening of cyclopropanes by Ag^+ has also ample precedents.[13] The reaction of some other siloxycyclopropanes with $AgBF_4$ are shown in Table I.

Table I. Reaction of Siloxycyclopropanes with $AgBF_4$ and $Cu(BF_4)_2$[a]

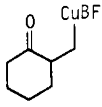
siloxycyclopropane	reagent	product	yield,[b] %
	$AgBF_4$ $Cu(BF_4)_2$		42 78
	$Cu(BF_4)_2$		81
	$AgBF_4$		68
	$AgBF_4$ $Cu(BF_4)_2$		68 77
	$AgBF_4$ $Cu(BF_4)_2$		70 87, 80
	$AgBF_4$ $Cu(BF_4)_2$		68 74
	$Cu(BF_4)_2$		69
	$Cu(BF_4)_2$		70
	$Cu(BF_4)_2$		63

[a] Reactions were performed on 1-5 mmol scale according to the procedure described in the text (for $AgBF_4$, −20 to ~15 °C, 0.5-1 h; for $Cu(BF_4)_2$, 15 °C, 0.5-1 h) with Et_2O as solvent. No efforts were made to establish the ratio of meso and racemic isomers concerning the products obtainable from bicyclic substrates. [b] Determined by GLC. Isolated yields are underlined.

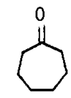
Interestingly, copper(II) tetrafluoroborate ($Cu(BF_4)_2$)[14] (7 mmol), less expensive and less hygroscopic than $AgBF_4$, also reacted with **4** (5 mmol) at 15 °C in Et_2O (5 mL) to give even higher yield of the same product, **7** (87% GLC and 80% isolated yields). Again the reaction was site selective at a in **4**. Table I also contains the results of the reaction of siloxycyclopropanes with $Cu(BF_4)_2$ in Et_2O at 15 °C.

Some characteristics of the present $Cu(BF_4)_2$-induced coupling may deserve comments. The diketone **7** was obtained in good yield in CH_3COOEt (86%) and even in protic solvents, such as EtOH (86%), *t*-BuOH (89%), and MeOH (37%).[15] When the reaction of **4** (1 mmol) was carried out using $^1/_2$ molar equiv of $Cu(BF_4)_2$ (0.5 mmol) in Et_2O (1 mL), a clean copper mirror gradually appeared on the surface of the reaction vessel, and **7** was obtained in 83% GLC yield. This implies that the Cu(II) salt can serve as two electron-oxidizing species through the overall process.

These results may be explained by assuming β-copper ketone **8** in a similar way as Scheme I.[16] Coupling of **8** would lead to the formation of **7** and $CuBF_4$, which in turn would disproportionate to $Cu(BF_4)_2$ and Cu(0). Any ideas that the cleavage of the C–C bond in **4** by Ag^+ or Cu^{++} would give free radical or cationic species seem unattractive, since such a process would give rise to more stable radical or cationic intermediate **9** as the results of central bond fission (cleave b in Scheme I).[17,18]



8



9

(* = · or +)

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[8] Obtained as a mixture of meso and racemic isomers: mp 74–79 °C; ms, *m/e* 222 (M^+), 204 ($M^+ - H_2O$); ^1H NMR (CCl_4, Me_4Si) δ 1.94–2.60 (m); ^{13}C NMR ($CDCl_3$) δ 213.06 (s, C=O), 50.91, 50.58 (each d, methine C α to C=O); IR (Nujol) 1700 cm^{-1}. A multistep and low overall yield synthesis of **7** has previously been reported. See: Ghera, E.; Gibson, M.; Sondheimer, F. *J. Am. Chem. Soc.* **1962**, *84*, 2953.

[9] It appears general that the ring opening of **4** occurs at the least hindered site; see for (a) bromination: Murai, S.; Seki, Y.; Sonoda, N. *J. Chem. Soc., Chem. Commun.* **1974**, 1032. (b) Isomerization with ZnI_2: Murai, S.; Aya, T.; Renge, T.; Ryu, I.; Sonoda, N. *J. Org. Chem.* **1974**, *39*, 858. Ryu, I.; Murai, S.; Otani, S.; Sonoda, N. *Tetrahedron Lett.* **1977**, 1995. (c) Mercuration: ref 6.

[10] Distilled out directly from the reaction mixture; ^1H NMR δ 0.21 (d, J_{HF} = 7 Hz).

[11] Alternatively, the $(CH_3)_3Si$ group in **4** might be converted to five coordinated $F(CH_3)_3Si^-$ group before the attack of Ag^+. At the present stage we can not eliminate the possibility that the reaction might proceed via prior formation of cyclopropoxy metal intermediates.

[12] (a) Whitesides, G. M.; Bergbreiter, D. E.; Kendall, P. E. *J. Am. Chem. Soc.* **1974**, *96*, 2806. (b) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1979; Chapter 10.

[13] Greenbery, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978. Paquette, L. A. *Acc. Chem. Res.* **1971**, *4*, 280.

[14] Purchased from Ventron Co. Prior to use, dried and stored over P_2O_5 under reduced pressure.

[15] The reaction of **4** with $AgBF_4$ can be also conducted by using protic solvent such as MeOH (-20 to ~15 °C, 0.5 h, 50% yield). For examples of silver salt induced coupling of alkyl moieties that proceeded in protic solvents (MeOH or H_2O), see: Brown, H. C.; Hebert, N. C.; Synder, C. H. *J. Am. Chem. Soc.* **1961**, *83*, 1001. Theile, H. *Z. Electrochem.* **1974**, *49*, 426.

[16] To our knowledge the related alkylcopper(II) species (RCu(II)X) analogous to that postulated here seem rare and have been postulated in the reaction of CuX_2 with organometallics (R_4Pb or RHgX). See: (a) Clinton, N. A.; Kochi, J. K. *J. Organomet. Chem.* **1972**, *42*, 241; *Ibid.* **1973**, *56*, 243. (b) Beletskaya, I. P.; Artamkina, Y. A.; Reutov, O. A. *Ibid.* **1975**, *99*, 343. An alternative mechanism via β-acylalkylcopper(I) may also be envisioned. $Cu(BF_4)_2$ could effect oxidative dimerization of β-acylalkylcopper(I) intermediates, if formed, from a siloxycyclopropane and $Cu(I)BF_4$ obtainable from $Cu(BF_4)_2$ and Cu(0). See: (a) Whitesides, G. M.; Stedronsky, E. R.; Casey, C. P.; Filippo, J. S., Jr., *J. Am. Chem. Soc.* **1978**, *92*, 1426. (b) Tamura, M.; Kochi, J. K. *J. Organomet. Chem.* **1972**, *42*, 205. (c) Reference 12b.

[17] (a) Ito, Y.; Fujii, S.; Saegusa, T. *J. Org. Chem.* **1976**, *41*, 2073; *Org. Synth.* **1980**, *59*, 113. (b) Schaafsma, S. E.; Jorritsma, R.; Steinberg, H.; de Boer, T. S. *Tetrahedron Lett.* **1973**, 827.

[18] The free radical pathway seems incompatible with the following observations: When the reaction was conducted in the presence of styrene or 2,3-dimethylbutadiene, any significant products with incorporation of these olefins were not formed. Furthermore, the reaction in the presence of *p*-cymene, a good hydrogen donor, did not affect the product distribution.

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Studies on the further use of intermediate **6** and **8** in synthesis as well as application of the β-metal ketone strategy to other naked (or ligand free) metal cations are in progress.

Acknowledgment. This work was supported in part by Grant-in-Aid for Special Project Research No. 57118002 provided by the Ministry of Education, Science, and Culture, Japan. We thank Shin-Etsu Chemical Industry Ltd. for the gift of trimethylchlorosilane.

Supplementary Material Available: Spectral data of products listed in Table I (7 pages). Ordering information is given on any current masthead page.

(Iminomethylidene)phosphines ($RP{=}C{=}NR$)

Curt Wentrup,*[1a] Horst Briehl,[1a] Gerd Becker,[1a,b]
Gudrun Uhl,[1a,b] Hans-Jürgen Wessely,[1a,b]
André Maquestiau,[1c] and Robert Flammang[1c]

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There has been much recent interest in compounds incorporating $P{=}C$[2,3] and $P{=}P$[4] double bonds. Furthermore, the stable (2,2-dimethylpropylidyne)phosphine, $(CH_3)_3CC{\equiv}P$, featuring a PC triple bond has been prepared.[5] However, previous attempts to isolate cumulenes possessing a two-coordinate phosphorus atom, $RP{=}C{=}X$, have failed,[2,3,6] except in a single case, the preparation of the stable and sterically protected $(CH_3)_3CP{=}C{=}NC(CH_3)_3$.[7] We now wish to report a general method of preparation of unstable (iminomethylidene)phosphines (monophosphorus analogues of carbodiimides), their direct observation by IR and mass spectrometry, and their initial chemical reactions.

The required starting materials, (iminomethyl)phosphines **1**, exist in equilibrium with carbamoylphosphines $[(CH_3)_3SiP(R)CON(Ph)Si(CH_3)_3]$ and smaller amounts of alkylidenephosphines $RP{=}C(OSi(CH_3)_3)N(Ph)Si(CH_3)_3$.[8] In analogy with the reaction used in the preparation of $(CH_3)_3CC{\equiv}P$,[5] the compounds **1** could be expected to eliminate hexamethyldisiloxane and thus give rise to the desired (iminomethylidene)phosphines, $RP{=}C{=}NPh$ (Scheme I).

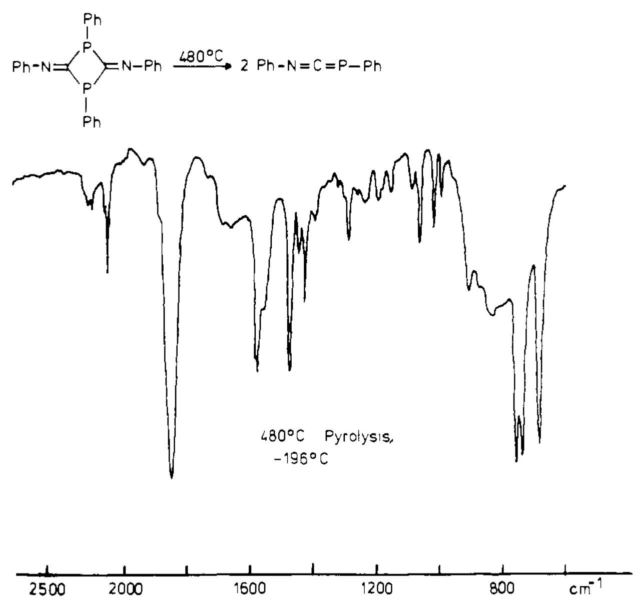
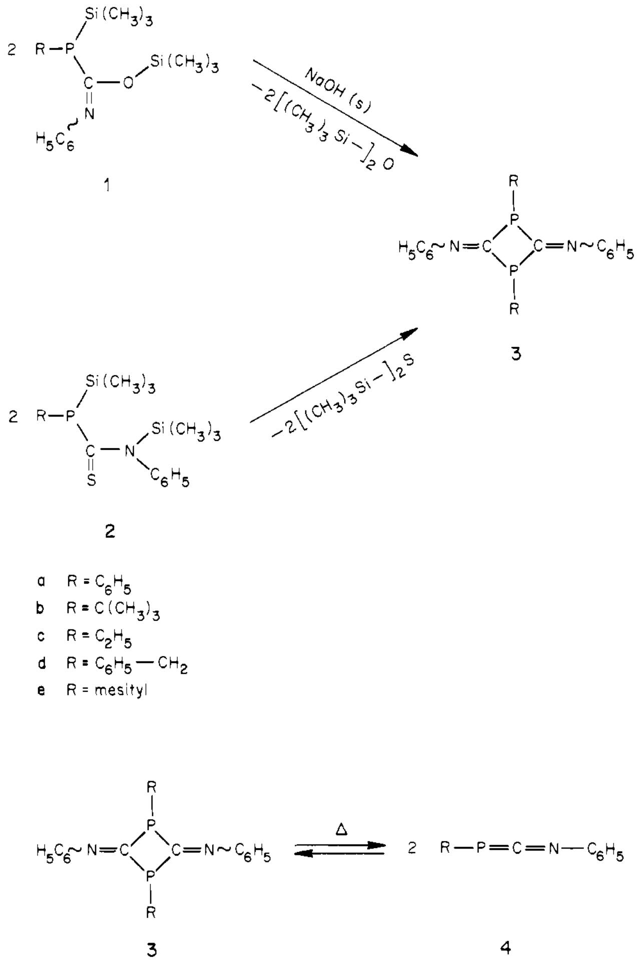


Figure 1. IR spectrum (−196 °C) of the product of pyrolysis of **3a** at 480 °C.

Scheme I



In the event, the treatment of **1** with a catalytic amount of solid NaOH led only to the isolation of the dimers **3**.[9] **3b** and **3e** were also obtained by spontaneous decomposition of the adducts **2b** and

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(9) (a) Satisfactory elemental analyses (C, H, N, P) were obtained for these compounds. (b) X-ray crystallographic determinations of **3c** and **3d** confirm the structure assignments. The two exocyclic phosphorus ligands are trans oriented. Full crystallographic data will be published: Becker, G.; Härer, J.; Riffel, H.; Uhl, G.; Wessely, H.-J., in preparation.

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