crystallographically imposed inversion symmetry. There are no short intermolecular contacts in the structure. The Cu–Cu distance is 4.908 (2) Å; other distances and angles are approximately as expected. The "$Cu(acac)_2$" (acacH = 2,4-pentanedione) moieties are essentially planar and make an angle of 89.8° with the bridging aromatic rings, giving the molecule approximate overall D_{2h} symmetry.

Additional details concerning electronic structure and reactivity for the complex may be seen from the electronic absorption spectra in Figure 2, taken on solutions of $Cu_2(m\text{-}XBA)_2$ in chloroform with and without added pyridine. Spectrum A, in pure chloroform, shows two d–d absorption bands with maxima at 518 (ϵ = 68) and 646 nm (ϵ = 73 M^{-1} cm^{-1}). These bands are very similar in energy to those for $Cu(acac)_2$ (λ_{max} = 532 (ϵ = 26) and 658 nm (ϵ = 34 M^{-1} cm^{-1})),[13] but about twice as intense. Thus, the copper atoms in $Cu_2(m\text{-}XBA)_2$ behave electronically much like isolated $Cu(acac)_2$ units. The room-temperature effective magnetic moment (Gouy method, powdered sample) for $Cu_2(m\text{-}XBA)_2$ of approximately 1.8 μ_B per copper atom suggests that the magnetic coupling between the copper atoms is also relatively weak.

Solutions of $Cu_2(m\text{-}XBA)_2$ change color from olive green to bright yellow-green on addition of pyridine (Figure 2B), and the principal d–d absorption now occurs at 635 nm. As estimated from spectral data at intermediate concentrations, the formation of the new species is essentially complete in 50% pyridine. The position and intensity (ϵ = 152 M^{-1} cm^{-1}) of the new band again compare favorably with those of $Cu(acac)_2(py)$ (py = pyridine) (λ_{max} = 654 nm; ϵ = 73 M^{-1} cm^{-1}).[14] This evidence, combined with the observation that the space between the copper atoms is to small to accommodate pyridine, leads to the formulation of the new species as $Cu_2(m\text{-}XBA)_2(py)_2$, with pyridine molecules in the axial positions L of **1**.

Evidence for association of solvent molecules with $Cu_2(m\text{-}XBA)_2$ comes from ^1H NMR data as well. Solutions of $Cu_2(m\text{-}XBA)_2$ in $CHCl_3/CDCl_3$ mixtures show significant broadening of the $CHCl_3$ resonance even for $[Cu_2(m\text{-}XBA)_2]$ values in the millimolar range. The effect is more pronounced for $CHCl_3$ than for Me_4Si under similar conditions, suggesting a specific outer-sphere interaction with chloroform. Broadening is also observed in solutions of $Cu_2(m\text{-}XBA)_2$ containing pyridine, the amount being greatest for the pyridine α protons.[15]

Thus, we have structurally and spectroscopically characterized the first cofacial binuclear complexes of simple bis(β-diketone) ligands. A more detailed study of EPR spectra and magnetic susceptibility of $Cu_2(m\text{-}XBA)_2$ is currently under way. We are also exploring the affinities of these and related complexes for small diatomic molecules G of **1** and the redox activity of the resulting adducts, as well as variations in these properties as a function of the bridging bis(β-diketone) ligand.

(13) The data for $Cu(acac)_2$, with absorption maxima and intensities calculated by deconvolution of the observed $CHCl_3$ spectra, are from: Belford, R. L.; Calvin, M.; Belford, G. *J. Chem. Phys.* **1957**, *26*, 1165.

(14) Graddon, D. P.; Schulz, R. A. *Aust. J. Chem.* **1965**, *18*, 1731. These workers resolved an additional absorption band (λ_{max} = 800 nm; ϵ = 32 M^{-1} cm^{-1}) in the $Cu(acac)_2(py)$ spectrum; a similar feature can be identified in the spectrum of Figure 2B here, although it is difficult to determine accurately its location and intensity. The authors in ref 13 assigned the band at 654 nm to the sum of two closely spaced bands, but the simpler approach is taken here.

(15) The formulation $Cu_2(m\text{-}XBA)_2(py)_2$, with axial ligation of pyridine to Cu, is consistent with the observed broadening of the pyridine resonances. For chloroform a more likely model is weak hydrogen bonding to the oxygen atoms of the ligand, as has been suggested for $Cu(acac)_2$: Kitaigorodskii, A. N.; Nekipelov, V. M.; Zamaraev, K. I. *J. Struct. Chem. (Engl. Transl.)* **1978**, *19*, 686. See also: Langford, C. H.; Stengle, T. R. In "NMR of Paramagnetic Molecules: Principles and Applications"; La Mar, G. N., Horrocks, W. D., Jr., Holm, R. H., Eds.; Academic Press: New York, 1973; p 372.

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Registry No. $Cu_2(m\text{-}XBA)_2$, 93040-31-4; $Cu_2(m\text{-}XBA)_2(py)_2$, 93040-33-6; *m*-XBA, 93040-32-5; $Cu(NH_3)_4^{2+}$, 16828-95-8.

Supplementary Material Available: Stereoscopic view of the unit cell (Figure 3) and listings of atomic positional and thermal parameters, interatomic distances and angles, and observed and calculated structure factors for $Cu_2(m\text{-}XBA)_2$ (14 pages). Ordering information is given on any current masthead page.

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Synthesis of Novel Organo(silyl)phosphine Synthons and Their Conversion to New Organophosphines

Sir:

Organo(silyl)phosphines [e.g., Me_3SiPR_2 and $(Me_3Si)_2PR$], because they contain highly reactive Si–P bonds, offer considerable potential for novel organophosphorus and organophosphorus–metal compound systhesis,[1] e.g. the recent preparation of $[Co_4(\mu_3\text{-}PPh)_4]$ from the reaction of $CoCl_2{\cdot}2PPh_3$ with $(Me_3Si)_2PPh$.[2] Unfortunately, because the available organo(silyl)phosphines have been limited to cases where R = alkyl or aryl,[3] the derived organophosphorus products have been limited. Recently, we have studied Me_3SiPH_2–olefin radical reactions and found they yield selectively and cleanly new classes of Me_3Si-substituted products. These synthons are converted hydrolytically to new primary and secondary phosphines, thus demonstrating a widely exploitable new two-step phosphine synthesis.

Reactions of Me_3SiPH_2[4] with the olefins **1–4** listed in Table I, in benzene or toluene at 85 °C and initiated by AIBN [AIBN = 2,2′-azobis(isobutyronitrile)], occur cleanly to yield the new silylphosphines, **5–8**. Hydrolysis of **5–8** by their reaction with excess (typically 20%) deoxygenated H_2O in benzene yields the primary and secondary organophosphines **9–12** quantitively. Products from both the phosphine–olefin and hydrolysis reactions were handled in vacuo and separated by low-temperature fractional distillation. Me_3SiPH_2 with excess 1,4-pentadiene (**1**) yields **5**; only tentative ^{31}P NMR spectral evidence was obtained for intermediate pentenyl(silyl)phosphine formation. Excess norbornadiene (**2**) with Me_3SiPH_2 yields intractable oligomeric/polymeric products; however, with excess Me_3SiPH_2, **6** predominates. Further conversion of **6** to $Me_3SiP(C_7H_9)_2$ is not observed. Di-

(1) Weber, W. P. "Silicon Reagents for Organic Synthesis"; Springer-Verlag: Berlin, 1983.

(2) Fenske, D.; Basoglu, R.; Hachgenei, J.; Rogel, F. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 160.

(3) See for example: (a) Clegg, W.; Haase, M.; Klingebiel, U.; Sheldrick, G. M. *Chem. Ber.* **1983**, *116*, 146. (b) Cowley, A. H.; Newmann, T. H. *Organometallics* **1982**, *1*, 1412. (c) Fritz, G.; Schaeffer, H.; Holderich, W. *Z. Anorg. Allg. Chem.* **1974**, *407*, 266. (d) Abel, E. W.; Illingworth, S. M. *Organomet. Chem. Rev. Sect. A* **1970**, *5*, 143.

(4) Me_3SiPH_2 is prepared as described previously: Norman, A. D. *Inorg. Chem.* **1970**, *9*, 870.

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Table I

olefin reactant	silylphosphine product (Me_3Si = R)	% conversion	% yield	hydrolysis product
 1	 5	64	90	 9
 2	 6	100	80	 10
 3	 7	100	>95	 11
 4	 8[a]	90	95	 12[a]

[a] Formed as cis and trans isomers.

phenyl(vinyl)phosphine (**3**) and Me_3SiPH_2 (2:1 mole ratio) yield **7**; only with excess Me_3SiPH_2 is the intermediate $Ph_2PCH_2CH_2PHSiMe_3$ obtained. Divinyl(phenyl)phosphine (**4**) with Me_3SiPH_2 yields **8**, with no indication of intermediate $PhP(CHCH_2)CH_2CH_2P(H)SiMe_3$ formation.

The new phosphines prepared herein (**5–8** and **10–12**) were characterized directly and, in the cases of **5–8**, secondarily by hydrolysis derivatization to the related primary or secondary phosphines. Compound **5** exhibits spectral properties[5] consistent with those reported for other substituted phosphorinanes[6] and is readily converted to the known **9**.[6,7] **6** is the first reported primary nortricylenylphosphine, exhibiting pairs of doublet resonances in the ^{31}P (δ −152, −148.8) and ^1H NMR spectra, due to two diastereomeric isomer pairs containing two chiral atom centers.[8] Compound **10**, obtained by hydrolysis of **6**, shows a single triplet ^{31}P NMR resonance,[9] the expected result of losing one chiral center upon conversion of **6** to **10**. The $^{13}C\{^1H\}$ NMR spectrum of **10** shows seven unique carbon resonances, six of which are split by coupling to phosphorus. The three lowest field resonances (δ 8.60, 11.21, 16.70) are in the region expected for carbon atoms of a cyclopropane ring, consistent with a nortricyclene structure. The PH_2 protons of **10** are diasterotopic and exhibit characteristic geminal coupling; the ^1H NMR spectral resonance is a doublet ($^1J_{PH}$ = 190 Hz) of methine proton-split ($^3J_{HH}$ = 6.4 Hz) AB patterns ($^2J_{HH}$ = 12.7 Hz). Homonuclear decoupling of the δ 1.58 methine resonance causes collapse to a pair of AB resonance patterns. Compound **7**, a tertiary triphosphine,[10] is converted upon hydrolysis to triphosphine **11**, which contains a central secondary and two terminal tertiary phosphorus atoms.[11] Compounds **8** and **12** are 1,4-diphosphacyclohexanes.[12,13] On the basis of correlation of their ^{31}P and ^1H NMR spectral data with literature data[14] for phosphorinanes, **8A/12A** and **8B/12B** are tentatively characterized as trans and cis isomers, respectively.

The Me_3SiPH_2–olefin reactions described herein allow limited conclusions about their use in new organo(silyl)phosphine syntheses. Like previously reported phosphine–olefin reactions,[15] addition of Me_3SiPH_2 to olefins appears to be exclusively anti-Markovnikov. Reactions in general are remarkably clean, more so than those of PH_3 or primary organophosphines (RPH_2).[15] Although of most interest in systems where unique products can be obtained by taking advantage of the "protecting" nature of the Me_3Si group, indications are that the two-step synthesis may be a general, useful method for preparation of conventional primary and secondary phosphines also. Studies of other silylphosphine–olefin reactions and use of new organo(silyl)phosphine synthons in other novel phosphorus compound syntheses are under investigation currently.

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Registry No. **1**, 591-93-5; **2**, 121-46-0; **3**, 2155-96-6; **4**, 26681-88-9; **5**, 88471-60-7; **6**, 92623-32-0; **7**, 92623-33-1; *cis*-**8**, 92623-34-2; *trans*-**8**, 92623-35-3; **9**, 4743-40-2; **10**, 92623-36-4; **11**, 92623-37-5; *cis*-**12**, 92623-38-6; *trans*-**12**, 92623-39-7; Me_3SiPH_2, 17446-52-5.

(5) **5**: $^{31}P\{^1H\}$ NMR (C_6D_6) δ −107.8 (s); $^{13}C\{^1H\}$ NMR (C_6D_6) δ −2.5 (d, J_{PC} = 11.0 Hz, area 3), 18.4 (d, J_{PC} = 14.6 Hz, area 2), 27.1 (d, J_{PC} = 3.7 Hz, area 2), 28.7 (d, J_{PC} = 9.9, area 1); ^1H NMR (C_6D_6) δ 0.3 (d, J_{PH} = 4.5 Hz, area 9), 2.3 (complex, area 10); characteristic IR (cm^{-1}) 445 m (Si–P); mass spectrum, parent at *m/e* 175, $^{12}C_8H_{19}{}^{29}SiP^+$. Anal. Calcd for $C_8H_{19}Si_{29}P$: C, 55.13; H, 10.99; P, 17.77. Found: C, 55.04; H, 10.81; P, 18.16.

(6) (a) Braid, M. Ph.D. Thesis, Temple University, 1962. (b) Lambert, J. B.; Oliver, S. L.; Jackson, G. F. *Tetrahedron Lett.* **1969**, *25*, 2027.

(7) **9**: $^{31}P\{^1H\}$ NMR (C_6D_6) δ −66.0 (s); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 17.2 (d, J_{PC} = 11.0 Hz, area 2), 26.2 (s, area 1), 27.8 (d, J_{PC} = 2 Hz, area 2); ^1H NMR (C_6D_6) δ 0.40–0.95 (complex, area 10), 3.10 (d of t, J_PH = 190 Hz, area 1); characteristic IR (cm^{-1}) 2287 vs (P–H); mass spectrum parent at *m/e* 102, $^{12}C_5H_{11}P^+$.

(8) **6**: $^{31}P\{^1H\}$ NMR (C_6D_6) δ −149.3 (s), −152.5 (s); ^1H NMR (C_6D_6) δ 0.2 (d, J_{PC} = 4.5 Hz, area 9), 0.25 (d, J_{PC} = 4.5, area 9), 0.8–1.8 (complex, area 18), 2.0 (d of m, J_{PH} = 191 Hz, area 1); characteristic IR (cm^{-1}) 3100 m (cyclopropyl CH), 2280 s (P–H), 470 m (Si–P); mass spectrum, parent at *m/e* 199, $^{12}C_{10}H_{19}{}^{29}SiP^+$. Anal. Calcd for $C_{10}H_{19}PSi$: C, 60.56; H, 9.66; P, 15.62. Found: C, 60.24; H, 9.55; P, 15.86.

(9) **10**: $^{31}P\{^1H\}$ NMR (C_6D_6) δ −142.7 (s); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 8.60 (s), area 1), 11.21 (d, J_{PC} = 4.6 Hz, area 1), 16.69 (d, J_{PC} = 5.4 Hz, area 1), 28.40 (d, J_{PC} = 5.8 Hz, area 1), 30.60 (d, J_{PC} = 8.0 Hz, area 1), 33.82 (d, J_{PC} = 5.0 Hz, area 1), 34.47 (d, J_{PC} = 8.8 Hz, area 1); ^1H NMR (C_6D_6) δ 0.9–1.8 (complex, area 9), 2.28 (d of m, J_{PH} = 190 Hz, area 2); characteristic IR (cm^{-1}) 2973 s (cyclopropyl C–H), 2300 vs (P–H), 1080vs (PH_2), 915 m (PH_2); mass spectrum parent at *m/e* 126, $^{12}C_7H_{11}P^+$.

(10) **7**: $^{31}P\{^1H\}$ NMR (C_6D_6) δ −13.4 (d, J_{PP} = 28.3 Hz, area 2), −85.9 (t, J_{PP} = 28.3 Hz, area 1); ^1H NMR (C_6D_6) δ 0.1 (d, J_{PH} = 28.3 Hz, area 2), −85.9 (t, J_{PP} = 28.3 Hz, area 1); ^1H NMR (C_6D_6) δ 0.1 (d, J_{PH} = 4.5 Hz, area 9), 1.4–2.5 (complex, area 8), 7.0–7.7 (complex, area 20). Owing to high hydrolytic instability, no elemental analysis was obtained.

(11) **11**: $^{31}P\{^1H\}$ NMR (C_7D_8) δ −14.0 (d, J_{PP} = 22 Hz, area 2), −58.1 (t, J_{PP} = 22 Hz, area 1); $^{13}C\{^1H\}$ NMR (C_7D_8) δ 16.7 (d of d, J_{PC} = 14.8 Hz, area 2), 27.0 (d of d, J_{PC} = 15.5 Hz, 9.4 Hz, area 2), 128.6 (s), 128.7 (s), 139.1 (d of d, J_{PC} = 18.6 Hz, 1.8 Hz); ^1H NMR (C_7D_8) δ 1.5–1.9 (complex, area 4), 3.1 (d of m, J_{PH} = 194 Hz, area 1), 7.1–7.7 (complex, are 20); characteristic IR (cm^{-1}) 2280 vs (P–H); mass spectrum parent at *m/e* 458, $^{12}C_{28}H_{29}P_3^+$.

(12) **8**: $^{31}P\{^1H\}$ NMR (C_6D_6) δ −25.5 (s) and −84.61 (s) [isomer A, area 1], −28.6 (d) and −82.30 (d, J_{PP} = 20.2 Hz) [isomer B, area 2.3]; ^1H NMR (C_6D_6) δ 0.30 (d, area 9, J_{PH} = 4.5 Hz), 1.3–2.4 (complex, area 8), 7.1–7.7 (complex, area 5); characteristic IR (KBr, cm^{-1}) 480 (Si–P); mass spectrum, parent at *m/e* 268, $^{12}C_{13}H_{22}P_2{}^{28}Si^+$. Owing to high hydrolytic instability, no elemental analysis was obtained.

(13) **12**: $^{31}P\{^1H\}$ NMR (C_7D_8) δ −27.4 (d) and −63.1 (d, J_{PP} = 3.3 Hz) [isomer A, area 1] −33.4 (d) and −58.3 (d, J_{PP} = 4.0 Hz) [isomer B, area 2]; $^{13}C\{^1H\}$ NMR (C_7D_8) δ 12.51 (d of d, J = 11.4 Hz, J = 1.5 Hz) and 28.96 (d of d, J = 12.3 Hz, J = 2.3 Hz [area 1, isomer A], 17.14 (d of d, J = 14.1 Hz, J = 11.1 Hz) and 23.19 (d, J = 16.2 Hz) [area 2, isomer B], 126.5–131.0 (complex, area 6, phenyl, isomers A and B); ^1H NMR δ 1.3–2.4 (complex, area 8), 7.1–7.7 (complex, area 5). Anal. Calcd. for $C_{10}H_{14}P_2$: C, 61.21; H, 7.19. Found: C, 61.08; H, 7.14.

(14) (a) Maryanoff, B. E.; McPhail, A. T.; Hutchins, R. O. *J. Am. Chem. Soc.* **1981**, *103*, 4432. (b) MacDonell, G. D.; Berlin, K. D.; Baker, J. R.; Ealick, S. E.; van der Helm, D.; Marsi, K. L. *J. Am. Chem. Soc.* **1978**, *100*, 4535.

(15) (a) Stiles, A. R.; Rust, F. R.; Vaughan, W. E. *J. Am. Chem. Soc.* **1952**, *74*, 3282. (b) Rauhut, M. M.; Currier, H. A.; Semsel, A. M.; Wystrach, V. P. *J. Org. Chem.* **1961**, *26*, 5138. (c) DuBois, D. L.; Meyers, W. H.; Meek, D. W. *J. Chem. Soc., Dalton Trans.* **1975**, 1011. (d) Meek, D. W.; Mazanec, T. J. *Acc. Chem. Res.* **1981**, *14*, 266. (e) Penkovskii, V. V. *Russ. Chem. Rev.* (*Engl. Transl.*) **1975**, 449.

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