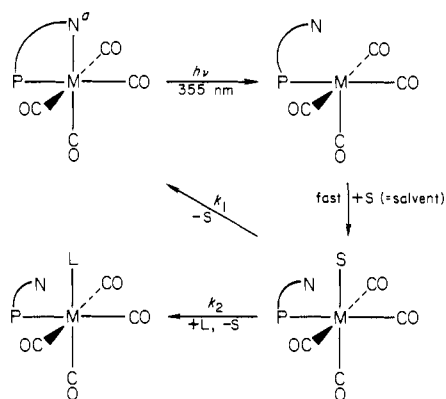


Scheme I

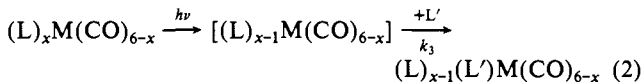


<sup>a</sup> N<sup>a</sup>P = 1-(diphenylphosphino)-2-(diethylamino)ethane; M = Cr, Mo.

more polar DCE. Such solvation is consistent with the observed interaction of solvents with such intermediates in low-temperature matrices.<sup>6</sup>

The relative magnitudes of  $k_1$  and  $k_2$  indicate a preference for unimolecular ring closure to bimolecular attack by L at the solvated intermediate. However, this preference is not as marked as might be expected on the basis of entropy considerations.<sup>7</sup> Relatively small ratios of  $k_1/k_2$ , determined for reactions in which a bidentate chelating ligand is thermally displaced by various Lewis bases, have been observed in a number of systems,<sup>8,9</sup> including (tmen)M(CO)<sub>4</sub> (tmen = N,N,N',N'-tetramethylethylenediamine; M = Cr, W) in their reactions with trialkyl phosphites.<sup>10</sup> Such abnormally small ratios have been attributed to distortions that are induced in the (chelate)M(CO)<sub>4</sub> complexes upon ring closure. In several instances the existence of such distortions has been demonstrated through X-ray structural determinations for the complexes.<sup>11</sup>

Rate constants for both pathways are significantly smaller (1-4 orders of magnitude) than are those that have been reported for bimolecular addition of L to intermediates produced via dissociation of a monodentate ligand from an octahedral complex,<sup>1,3</sup>



This observation further suggests a barrier to ring reclosure and also indicates that there may be significant steric interactions between L and the free end of the bidentate in the path governed by  $k_2$  (Scheme I). These possibilities are under continuing investigation.

**Acknowledgment.** The support of this research by the Robert A. Welch Foundation under Grant B-434 and by the North Texas State University Faculty Research Fund is gratefully acknowledged. The pulsed laser flash photolysis experiments and analyses of the data produced were performed at the Center for Fast Kinetics Research (CFKR) at the University of Texas at Austin.

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**Registry No.** I (M = Cr), 18040-40-9; I (M = Mo), 14971-44-9; II (M = Cr), 86273-14-5; II (M = Mo), 86273-15-6; *cis*-( $\eta'$ -NP)(P(OPr-*i*))<sub>3</sub>Cr(CO)<sub>4</sub>, 86273-16-7; *cis*-( $\eta'$ -NP)(P(OPr-*i*))<sub>3</sub>Cr(CO)<sub>4</sub>, 86273-17-8.

## Synthesis and Structure of a Diarsene: The First Compound with an Unsupported Arsenic-Arsenic Double Bond

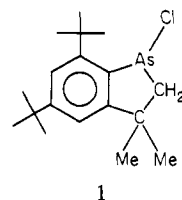
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The preparation and properties of diphosphenes (RP=PR) are subjects that have attracted the recent attention of several research groups.<sup>1</sup> We now report that by judicious choice of bulky ligands it is possible to isolate compounds featuring double bonds to arsenic.

Our initial approach to diarsene (RAs=AsR) synthesis involving the reductive coupling of (2,4,6-(*t*-Bu)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)AsX<sub>2</sub> was unsuccessful. The reaction of 2,4,6-(*t*-Bu)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>Li with 1 equiv of AsCl<sub>3</sub> in THF at -78 °C afforded the heterocycle **1** (mp 146-148 °C)<sup>2</sup> rather than (2,4,6-(*t*-Bu)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)AsCl<sub>2</sub> due to attack

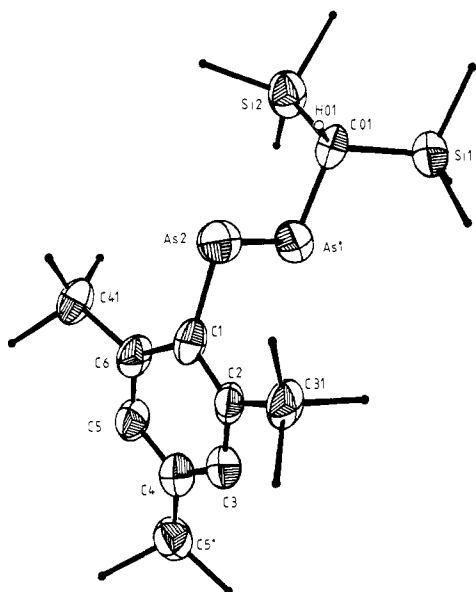


of As on an ortho *t*-Bu group. Although (2,4,6-(*t*-Bu)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)AsF<sub>2</sub> (**2**) (mp 119-121 °C)<sup>2</sup> can be prepared via the reaction of 2,4,6-(*t*-Bu)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>Li with AsF<sub>3</sub> (THF, -78 °C), **2** fails to yield a diarsene upon treatment with sodium naphthalene. However, **2** can be reduced to (2,4,6-(*t*-Bu)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)AsH<sub>2</sub> (**3**) (mp 146 dec)<sup>2</sup> by using LiAlH<sub>4</sub> in THF, and treatment of **3** with an equimolar quantity of (Me<sub>3</sub>Si)<sub>2</sub>CHAsCl<sub>2</sub><sup>3</sup> and a 5% excess of DBU (1,5-diazabicyclo[5.4.0]undec-5-ene) at 0 °C in THF solution resulted in a white precipitate and an orange-colored supernatant liquid. Filtration followed by chromatographic purification (silica gel/*n*-hexane) afforded a 72% yield of orange crystalline (2,4,6-(*t*-Bu)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)As=AsCH(SiMe<sub>3</sub>)<sub>2</sub> (**4**) (mp 110-113 °C). Preliminary characterization of **4**, the first compound with an unsupported arsenic-arsenic double bond,<sup>4</sup> was accomplished by high-resolution mass spectrometry (HRMS) (M<sup>+</sup> calcd, 554.1726;

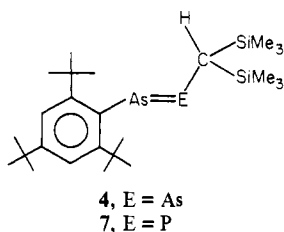
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(2) Analytical and spectroscopic data for this compound will be reported in a subsequent full paper.

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**Figure 1.** View of the (2,4,6-(*t*-Bu)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)As=AsCH(SiMe<sub>3</sub>)<sub>2</sub> (**4**) molecule. The methyl carbons are of reduced size for clarity. Important parameters: As(1)–As(2) 2.224 (2), As(1)–C(01) 1.976 (10), As(2)–C(1) 1.946 (10) Å; As(2)–As(1)–C(01) 99.9 (3)°, As(1)–As(2)–C(1) 93.6 (3)°.



found, 554.1745) and UV spectroscopy ( $\lambda_{\max}$  255 ( $\epsilon$  12660), 368 ( $\epsilon$  6960), and 449 nm ( $\epsilon$  180)) Confirmation of the structure of **4** was provided by a single-crystal X-ray diffraction study.<sup>5</sup> Like the congeneric diphosphenes, [(Me<sub>3</sub>Si)<sub>3</sub>C]<sub>2</sub>P<sub>2</sub> (**5**)<sup>6</sup> and (2,4,6-(*t*-Bu)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>P<sub>2</sub> (**6**),<sup>1a</sup> **4** adopts a trans geometry (Figure 1) and the skeletal atoms (C(01), As(1), As(2), and C(1)) are planar within experimental error (0.017 Å). The arsenic–arsenic distance in **4** (2.224 (2) Å) is the shortest such distance reported.<sup>7,8</sup>

(4) No unsupported arsenic–arsenic double bonds have been reported previously. Metal complexes of the type RAs–AsR–M are known, however. See: (a) Elmes, P. S.; Leverett, P.; West, B. O. *J. Chem. Soc., Chem. Commun.* **1971**, 747. (b) Huttner, G.; Schmid, H.-G.; Frank, A.; Oraina, O. *Angew. Chem., Int. Ed. Engl.* **1976**, 158 234.

(5) Crystal data for **4**: C<sub>25</sub>H<sub>48</sub>As<sub>2</sub>Si<sub>2</sub>, *M* = 554.17, triclinic, space group P1 (No. 2) (by refinement); *a* = 9.955 (9), *b* = 10.393 (7), *c* = 15.159 (5) Å;  $\alpha$  = 89.56 (4)°,  $\beta$  = 85.39 (6)°,  $\gamma$  = 78.31 (9)°; *U* = 1530 (3) Å<sup>3</sup>, *D<sub>c</sub>* = 1.199 g cm<sup>-3</sup>, *Z* = 2,  $\lambda$ (Mo K $\alpha$ ) = 0.71069 Å,  $\mu$ (Mo K $\alpha$ ) = 22.6 cm<sup>-1</sup>. From a total of 5046 unique reflections, measured on an Enraf-Nonius CAD-4 diffractometer over the range 2.0  $\leq$   $2\theta$   $\leq$  50.0°, 2508 (*I*  $>$  2.5 $\sigma$ (*I*)) were used to solve (Patterson and difference Fourier) and refine (full matrix, least squares) the structure of **4**. No absorption correction was applied. All non-hydrogen atoms were refined by using anisotropic thermal parameters while H(01) was positionally refined with a fixed isotropic temperature factor. Refinement with unit weights converged smoothly to give final residuals *R* = 0.0807, *R<sub>w</sub>* = 0.1062. Since the crystal quality was relatively poor, the percentage of observed data was somewhat low, causing rather high residuals and some difficulties with the refinement of one carbon atom (C(33)).

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(8) The arsenic–arsenic single bond length is 2.43–2.46 Å. See: (a) Maxwell, L. K.; Hendricks, S. B.; Mosely, V. M. *J. Chem. Phys.* **1935**, *3*, 699. (b) Burns, J. H.; Waser, J. *J. Am. Chem. Soc.* **1957**, *79*, 859. (c) Hedberg, K.; Hughes, E. W.; Waser, J. *Acta Crystallogr.* **1961**, *14*, 369. (d) Rheingold, A. L.; Sullivan, P. J. *Organometallics* **1983**, *2*, 327.

and is consistent with the value of  $\sim$ 2.3 Å that Dahl et al.<sup>7a,b</sup> have suggested for the arsenic–arsenic double bond. The bond angles at arsenic (99.9 (3)° at As(1); 93.6 (3)° at As(2)) are appreciably smaller than the bond angles at phosphorus in the diphosphenes **5** (108.5 (4)° av)<sup>6</sup> and **6** (102.8 (1)°),<sup>1a</sup> reflecting both the tendency to increasing *p* character in the ligand bonds as group 5A in descended and possibly a decrease in steric forces resulting from a lengthened double bond.

The primary arsine, **3**, also proved useful for the synthesis of a phospharsene (RP=AsR). Thus, treatment of an equimolar quantity of **3** and (Me<sub>3</sub>Si)<sub>2</sub>CHPCl<sub>2</sub><sup>3</sup> in THF solution at 0 °C in the presence of a 5% excess of DBU afforded orange-crystalline (Me<sub>3</sub>Si)<sub>2</sub>CHP=As(2,4,6-(*t*-Bu)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) (**7**) (mp 118–120 °C) after purification as per **4**. Compound **7** was characterized spectroscopically: HRMS, *M*<sup>+</sup> calcd 510.2248, found 510.2256; UV  $\lambda_{\max}$  254 ( $\epsilon$  10440), 354 ( $\epsilon$  8400), and 431 ( $\epsilon$  220). The 32.384-MHz <sup>31</sup>P{<sup>1</sup>H} NMR spectrum exhibited a very low-field resonance (*s*,  $\delta$  533), which is characteristic of double-bonded phosphorus compounds.<sup>1</sup>

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**Registry No.** **1**, 86528-35-0; **2**, 86528-36-1; **3**, 86528-37-2; **4**, 86528-38-3; **7**, 86528-39-4; 2,4,6-(*t*-Bu)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>Li, 35383-91-6; AsCl<sub>3</sub>, 7784-34-1; AsF<sub>3</sub>, 7784-35-2; (Me<sub>3</sub>Si)<sub>2</sub>CHAsCl<sub>2</sub>, 76505-21-0; (Me<sub>3</sub>Si)<sub>2</sub>CHPCl<sub>2</sub>, 76505-20-9.

**Supplementary Material Available:** Tables of bond lengths, bond angles, atomic coordinates, and thermal parameters (6 pages). Ordering information is given on any current masthead page.

## Elemental Sulfur and Selenium Induced Intramolecular Carbyne–Carbyne Coupling in Trinuclear Bis(carbyne) Cobalt Clusters. A Novel Entry into Metalladithiolenes and Metalladiselenolenes

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Sulfur is not only an undesirable pollutant in coal<sup>1</sup> and petroleum<sup>2</sup> but is also detrimental to fuel-related catalytic processes, such as hydrocarbon reforming<sup>2</sup> and Fischer–Tropsch synthesis.<sup>3</sup> While homogeneous transition-metal complexes have been studied as potential models<sup>4</sup> for hydrodesulfurization processes<sup>5</sup> and for sulfur–sulfur interactions,<sup>6</sup> none have specifically probed the reactivity of sulfur with respect to carbon-based potential surface analogues. We report that  $\mu_3$ - $\eta^1$ -carbyne ligands couple intramolecularly in the coordination sphere of trinuclear cobalt clusters when exposed to elemental sulfur (and selenium) to provide a

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