Scheme I

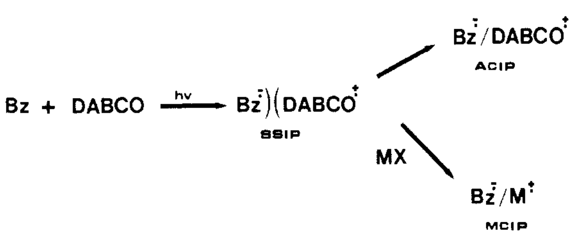

Table I. Heats of Reaction of the Photoreduction of Benzophenone by DABCO[a]

| solvent | added salt | $\Delta H_r$,[b] kcal/mol |
|---|---|---|
| acetonitrile | none | 52.0 |
| | $LiClO_4$ | 46.7 |
| | $NaClO_4$ | 47.7 |
| | $(n\text{-}Bu)_4NClO_4$ | 52.0 |
| ethanol | none | 48.5 |

[a] 337-nm excitation, ~0.2 OD, 0.1 M DABCO, 0.5 M salt, 298 K. [b] Values ±1.0 kcal/mol, $\Delta H_r$ is the enthalpy difference between the corresponding ion pair and initial reactants.

$\Delta H_r$, Table I, is determined by deconvolution of the photoacoustic waveform obtained from photolysis of the sample. The standard employed as the transducer wave was ferrocene.[7] The $\Delta H_r$ values measured in acetonitrile correspond to the energy of the ACIP without added alkali metal salts and the MCIP with added alkali metal salts.[10] The energy of the hydrogen bonded ion pair is given by $\Delta H_r$ in ethanol.[11]

The energies of the ion pairs in acetonitrile are ordered, $E(Li^+) < E(Na^+) < E((n\text{-}Bu)_4N^+) \simeq E(\text{no salt})$, Table I. The lower energies of the $Na^+$ and $Li^+$ ion pairs are not due to an increase in ionic strength but rather to specific ionic interactions because the addition of the nonassociating salt $(n\text{-}Bu)_4NClO_4$ did not lower the energy of the ACIP.[12] The difference of only 1 kcal/mol in the ion pair energies for $Li^+$ and $Na^+$ is somewhat surprising since normally $Li^+$ is considered to bind more strongly, via Coulombic attraction, than $Na^+$ due to the smaller ionic radius of $Li^+$. However, the 1 kcal/mol does not reflect the absolute difference in binding between the two cations with the radical anion of benzophenone. Rather, these measurements reflect only the difference in binding energies of the cation with the organic anion and the solvent, acetonitrile.

The free energy change, $\Delta G$, from ground-state reactants to the ACIP, can be estimated from the Rehm–Weller equation,[2]

$$\Delta G = 23.06(E_{1/2}{}^{\text{ox}} - E_{1/2}{}^{\text{red}}) - e^2/(\epsilon r)$$

where $E_{1/2}{}^{\text{ox}}$ is the oxidation potential of DABCO, $E_{1/2}{}^{\text{red}}$ is the reduction potential of benzophenone, $\epsilon$ is the dielectric constant of the medium, and $r$ is the encounter distance of the ion pair. Redox potentials of DABCO and benzophenone were measured in acetonitrile,[13] and the difference, $E^{\text{ox}} - E^{\text{red}} = 2.47$ eV, is in accord with literature values.[14] By use of this difference, $\epsilon = 37.5$[15] and $r = 2.9$ Å,[16] the above equation gives $\Delta G \simeq 54$ kcal/mol. The calculated and experimental heats of reaction are in good agreement if the entropy of formation of the ion pair is small.[17] Similarly, in ethanol, using $E^{\text{ox}} - E^{\text{red}} = 2.17$ eV from literature redox potentials,[18] $\Delta G \simeq 50$ kcal/mol which agrees well with the experimental value.[19]

The resonable agreement between the calculated and experimental values suggests that the term $e^2/(\epsilon r)$ is small and, in particular, that $\epsilon$ is large. Consequently, the argument that the macroscopic dielectric constant at large $r$ decreases to the square of the index of refraction as $r$ becomes small appears invalid when applied to the above Rehm–Weller equation.[20]

In summary, quantitative measurements of the stabilizing effect of alkali metals and the consequent driving force for the formation of the MCIP in the photoreduction of benzophenone have been determined by photoacoustic calorimetry. In addition, the experimental enthalpies support the use of the Rehm–Weller equation to estimate the ion pair energies of the ACIP.

**Acknowledgment.** This work was supported by the NSF (CHE-8418611). K.S.P. acknowledges support from the Alfred P. Sloan Foundation and the Henry and Camille Dreyfus Foundation for a teacher–scholar grant. J.L.G. acknowledges generous support from an NIH postdoctoral fellowship. We thank Prof. C. Koval for conducting the electrochemical measurements.

**Registry No.** Bz, 119-61-9; DABCO, 280-57-9.

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(9) The volume change for a photochemical reaction, $\Delta V$, may contribute to the observed acoustic wave. In this case, the negative $\Delta V$ of reaction would give a seemingly large value for $\Delta H_r$. However, the volume change in organic solvents should not significantly increase the acoustic signal so the stated enthalpies should be an upper limit.

(10) The equilibrium structure of the perchlorate alkali metal salts in acetonitrile is the solvent-separated ion pair.[6] Consequently, the enthalpy contribution to unpair the ions is believed to be small.

(11) On the time scale of the laser experiment, ~1 μs, decay of the ion pairs is slow and consequently does not contribute significantly to the overall enthalpy or reaction. However, deconvolution of the waveforms can be performed to account for this slow decay.[7] The decays of the ACIP and the $Na^+$ and $Li^+$ ion pairs in acetonitrile are approximately 15, 20, and 30 μs, respectively.

(12) The lack of increased stabilization of the ACIP with the addition of $(n\text{-}Bu)_4ClO_4$ may be anticipated from the absence of any significant salt effect on solvolysis rates in acetonitrile, i.e., small $b$ value.[3a]

(13) Cyclic voltammogram parameters at 298 K: ca. $10^{-3}$ M Bz, $10^{-3}$ M DABCO, 0.2 M $TBABF_4$ in $CH_3CN$, vs. $Ag/AgNO_3$ (0.1 M), $TBABF_4$ (0.5 M). Sweep rate from 50 to 1 V/s.

(14) (a) McKinney, T. M.; Geske, D. H. *J. Am. Chem. Soc.* **1965**, *87*, 3013. (b) Loutfy, R. O.; Loutfy, R. O. *J. Phys. Chem.* **1973**, *77*, 336.

(15) Reichardt, C. "Solvent Effects in Organic Chemistry"; Verlag Chemie: New York, 1979; p 270.

(16) Pauling, L. "Nature of the Chemical Bond"; Cornell University: Ithaca, NY, 1960.

(17) If we assume the entropy of formation, derived by Weller,[2b] of an exciplex to be −18 eu as the upper limit, then the estimated $\Delta H_r$ value from the Weller equation is ~49 kcal/mol.

(18) (a) Smith, J. R.; Masheder, D. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1732. (b) Kalinowski, M. K.; Grabowski, Z. R.; Pakula, B. *J. Chem. Soc., Faraday Trans.* **1966**, *62*, 918.

(19) In ethanol, the encounter distance of the hydrogen bonded ion pair is believed to be large, so the $e^2/(\epsilon r)$ term is negligible, i.e., ~0.

(20) Sadek, H.; Fuoss, R. M. *J. Am. Chem. Soc.* **1954**, *76*, 5905.

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# Mixed Valence, Phosphine Stabilized Sulfido Clusters of the Transition Metals: Synthesis and Structure of $Cr_3(\mu_3\text{-}S)_2(\mu_2\text{-}S)_3(dmpe)_3$, Cr(III,III,IV) (dmpe = Bis(1,2-dimethylphosphino)ethane). A Structurally Characterized $Cr_3$ Cluster

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*Received September 3, 1985*

The relevance of complexes containing transition-metal–sulfur bonds to biological systems[1] as well as to industrially important

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(1) Newton, W. E., Otsuka, S., Eds. "Molybdenum Chemistry of Biological Significance"; Plenum Press: New York, 1980. Lovenberg, W., Ed. "Iron-Sulfur Proteins"; Academic Press: New York, 1973, Vol. 1; 1974, Vol. 2; 1976, Vol. 3. Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1; *Proc. Natl. Acad. Sci. U.S.A.* **1973**, *70*, 988. Shah, V. K., Brill, W. J. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 3249. Coucovanis, D. *Acc. Chem. Res.* **1981**, *14*, 201. Eisenberger, P.; Kinkaid, B. M. *Science (Washington, D.C.)* **1978**, *200*, 1441. Sola, T.; Do, Y.; Berg, T. M.; Holm, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 7784. Do, Y.; Simhon, E. D.; Holm, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 6731. Draganjac, M.; Coucouvanis, D. *J. Am. Chem. Soc.* **1983**, *105*, 139.

reactions[2] is now well recognized. However, virtually all sulfido clusters so far reported bear either CO, Cp, or other anionic ligands such as $SR^-$ or halide.[3] We report here the synthesis and X-ray crystal structure of $Cr_3(\mu_3\text{-}S)_2(\mu_2\text{-}S)_3(dmpe)_3$ (**1**) (dmpe = bis(1,2-dimethylphosphino)ethane). This complex is particularly noteworthy since it is the first example of an early-transition-metal sulfido cluster stabilized only by phosphine ligands, until this report, known only for the late transition metals.[3] In addition, **1** is a rare example of a structurally characterized $Cr_3$ cluster. Very few chromium clusters are known, most of them bear CO or Cp and have either bridging or capping O and/or S atoms.[4] There are also a number of heterometallic cluster complexes which contain Cr.[5] In addition there are also a number of polynuclear chromium complexes such as the oxo-centered basic carboxylates, recently described by Cotton and co-workers, in which relatively long Cr–Cr distances indicate little significant metal–metal bonding.[6]

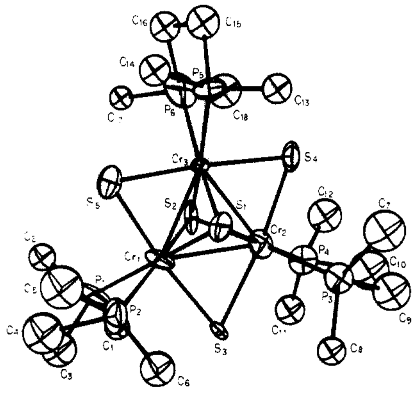

**Figure 1.** ORTEP view of **1**. Key bond lengths and angles are noted in the text.

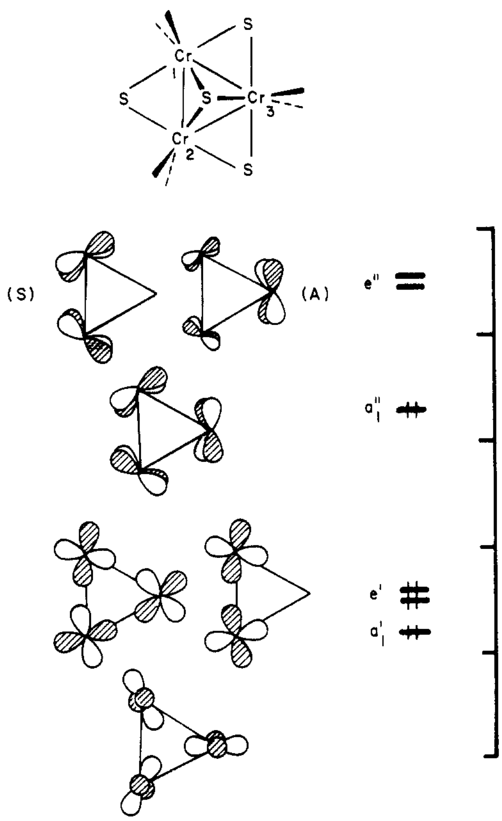

**Figure 2.** Top view of the valence, metal-centered orbitals in $Cr_3S_5(PH_3)_6$ at a $D_{3h}$ geometry. The energy scale on the right side of this figure is divided into 0.5-eV intervals.

The reaction of anhydrous $CrCl_2$ with NaSH (1:2) in methanol at −78 °C gives an immediate black suspension. Addition of excess dmpe (ca. 2 equiv per Cr) and warming slowly to room temperature over ca. 12 h gives a mixture consisting of a black precipitate and a brown solution. Deep purple, almost black, crystalline **1** may be isolated following evaporation to dryness and recrystallization of the residue from toluene at −20 °C. An insoluble black pyrophoric powder remains after the toluene extraction and this is thought to be Cr metal. Interestingly reverse addition of dmpe and NaSH gives *trans*-$Cr(SH)_2(dmpe)_2$ in high yield. This will be described elsewhere.[7] **1** is sparingly soluble in toluene, THF, $Me_2SO$, and MeOH. It is insoluble in hexane and appears to decompose in $CH_2Cl_2$. It appears to be air stable in the solid state and also in solution, at least for several hours. NMR data ($^1H$ and $^{31}P$) for **1** show only the presence of coordinated dmpe ($^{31}P\{^1H\}$ $\delta$ 48.83 s, free dmpe, $\delta$ −46.10).[8]

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(2) See, for example: Chisholm, M. H.; Corning, J. F.; Huffman, J. C. *Inorg. Chem.* **1982**, *21*, 286. Henkel, G.; Tremel, W.; Krebs, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 318. Rauchfuss, T. B.; Weatherill, T. D.; Wilson, S. R.; Zebrowski, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 6508. Bolinger, C. M.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 6321. Williams, P. D.; Curtis, M. D.; Duffy, D. N.; Butler, W. M. *Organomet.* 1983 *2*, 165. Shaver, A.; McCall, J. M.; Bird, P. H.; Ansari, N. *Organometallics* **1983**, *2*, 1894. Seyferth, D.; Hanes, B. W.; Rucker, T. G.; Cowie, M.; Dickson, R. S. *Organometallics* **1983**, *2*, 472. Wiggins, R. W.; Huffman, J. C.; Christou, G. *J. Chem. Soc., Chem. Commun.* **1983**, 1313. Wall, K. L.; Folting, K.; Huffman, J. C.; Wentworth, R. A. D. *Inorg. Chem.* **1983**, *22*, 2366. Kamata, M.; Hirotsu, K.; Higuchi, T.; Kido, M.; Tatsumi, K.; Yoshida, T.; Otsuka, S. *Inorg. Chem.* **1983**, *22*, 2416. Miller, W. K.; Haltiwanger, R. C.; VanDerveer, M. C.; Rakowski-DuBois, M. *Inorg. Chem.* **1983**, *22*, 2973. Chu, C. T. W.; Gall, R. S.; Dahl, L. F. *J. Am. Chem. Soc.* **1982**, *104*, 737.

(3) Recent exceptions: sulfido clusters with phosphine ligands; $[Ni_3(\mu_3\text{-}X)_2(PR_3)_6]^{2+}$ (R = Me, X = S; R = Et, X = S, Se) and $[Ni_9(\mu_4\text{-}S)_3(\mu_3\text{-}S)_6(PEt_3)_6]^{2+}$ (Cecconi, F.; Ghilardi, C. A.; Midollini, S. *Inorg. Chem.* **1983**, *22*, 3802) $[Co_6(\mu_3\text{-}S)_8(PEt_3)_6]BPh_4$ (Cecconi, F.; Ghilardi, C. A.; Midollini, S. *Inorg. Chim. Acta. Lett.* **1982**, *64*, L47. See also, for $Zr_3(S)(t\text{-}BuS)_{10}$ Coucouvanis, D.; Hadjikyriacou, A.; Kanatzidis, M. G. *J. Chem. Soc., Chem. Commun.* **1985**, 1224. For the linear Cr(III) trimer $(PPh_4)_2Na[Cr_3(SCH_2CH_2O)_6]$: Nicholson, J. R.; Wang, R. J.; Huffman, J. C.; Christou, G.; Chang, H. R.; Hendrickson, D. N. *J. Chem. Soc., Chem. Commun.* 1985, 1781.

(4) The complex $\{S[Cr(CO)_4]_3\}^{2-}$ was recently described and the structure has been reported: Darensbourg, D. J.; Zalewski, D. J. *Organometallics* **1984**, *3*, 1598; National Meeting of the American Chemical Society, Chicago, IL, Sept 1985; INOR 238. See also: Simmon, G. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1973**, *95*, 2164. Bottomley, F.; Paez, D. E.; White, P. S. *J. Am. Chem. Soc.* **1981**, *103*, 5581; **1982**, *104*, 5651. Bottomley, F.; Grein, F. *Inorg. Chem.* **1982**, *21*, 4170. Hoefler, M.; Tebbe, K.-F.; Veit, H.; Weiler, N. E. *J. Am. Chem. Soc.* **1983**, *105*, 6338. Pasynskii, A. A.; Eremenko, I. L.; Orazsakhatov, B.; Gasanov, G. Sh.; Shklover, V. E.; Struchkov, Yu. T. *J. Organomet. Chem.* **1984**, *269*, 147. Pasynskii, A. A.; Eremenko, I. L.; Rakitin, Yu. V.; Novotortsev, V. M.; Ellert, O. G.; Kalinnikov, V. T.; Shklover, V. E.; Struchkov, Yu. T.; Lindeman, S. V.; Kurbanov, T. Kh.; Gasanov, G. Sh. *J. Organomet. Chem.* **1983**, *248*, 309. Eremenko, I. L.; Pasynskii, A. A.; Gasanov, G. Sh.; Bagirov, Sh. A.; Ellert, O. G.; Novotortsev, V. M.; Kalinnikov, V. T.; Struchkov, Yu. T.; Shklover, V. E. *Izv. Akad. Nauk, SSSR, Ser. Khim.* **1983**, *6*, 1445.

(5) Pasynskii, A. A.; Eremenko, I. L.; Gasanov, G. Sh.; Orazsakhatov, B.; Shklover, V. E.; Struchkov, Yu. T. *Koord. Khim.* **1984**, *10*, 634. Pasynskii, A. A.; Eremenko, I. L.; Gasanov, G. Sh.; Struchkov, Yu. T.; Shklover, V. E. *J. Organomet. Chem.* **1984**, *276*, 349. Pasynskii, A. A.; Eremenko, I. L.; Gasnov, G. Sh.; Ellert, O. G.; Novotortsev, V. M.; Kalinnikov, V. T.; Struchkov, Yu. T.; Snklover, V. E. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1983**, *6*, 1446. Eremenko, I. L.; Pasynskii, A. A.; Orazsakhatov, B.; Ellert, O. G.; Novotortsev, V. M.; Kalinnikov, V. T.; Porai-Koshits, M. A.; Antsyshkina, A. S.; Dikareva, L. M.; Ostrikova, V. N.; Struchkov, Yu. T.; Gerr, R. G. *Inorg. Chim. Acta* **1983**, *73*, 225. Pasynskii, A. A.; Eremenko, I. L.; Ellert, O. G.; Novotortsev, V. M.; Rakitin, Yu. V.; Kalinnikov, V. T.; Shklover, V. E.; Struchkov, Yu. T. *J. Organomet. Chem.* **1982**, *234*, 315. Brunner, H.; Wachter, J. *J. Organomet. Chem.* **1982**, *240*, C41. Pasynskii, A. A.; Eremenko, I. L.; Orazsakhatov, B.; Kalinnikov, V. T.; Aleksandrov, G. G.; Struchkov, Yu. T. *J. Organomet. Chem.* **1981**, *216*, 211. Pasynskii, A. A.; Eremenko, I. L.; Orazsakhatov, B.; Rakitin, Yu. V.; Novototsev, V. M.; Ellert, O. G.; Kalinnikov, V. T.; Aleksandrov, G. G.; Struchkov, Yu. T. *J. Organomet. Chem.* **1981**, *214*, 351. Pasynskii, A. A.; Eremenko, I. L.; Orazsakhatov, B.; Kalinnikov, V. T.; Aleksandrov, G. G.; Struchkov, Yu. T. *J. Organomet. Chem.* **1981**, *214*, 367. Jund, R.; Lenoine, P.; Gross, M.; Bender, R.; Braunstein, P. *J. Chem. Soc., Chem. Commun.* **1983**, 86.

(6) See, for example: Cotton, F. A.; Wenning, W. *Inorg. Chem.* **1982**, *21*, 2675 and references therein.

(7) Also prepared by similar routes are isostructural *trans*-$M(SH)_2(dmpe)_2$, where M = Fe, Co: Arif, A. M.; Hefner, J. G.; Jones, R. A., manuscript in preparation.

The structure of **1** has been determined by X-ray crystallography.[9] **1** crystallizes in the orthorhombic space group $Pna2_1$ with four molecules per unit cell. An ORTEP view of the molecule is shown in Figure 1. There are several interesting features. The molecular structure consists of a $Cr_3$ triangle capped on each face by a $\mu_3$-S atom with three edge bridging $\mu_2$-S atoms. The Cr-($\mu_2$-S)$_3$ core is virtually planar[10] while the two $\mu_3$-S atoms are almost equally positioned above and below this plane (1.774 Å, av).[10] Each Cr atom bears a bidentate chelating dmpe ligand resulting in an overall distorted octahedral coordination geometry. There is a distinct deviation from an idealized $D_{3h}$ symmetry which can be attributed to a Jahn–Teller distortion (see below). The distortion is reflected in the Cr–Cr and Cr–S distances. Thus Cr(1)–Cr(2) is notably longer than either Cr(1)–Cr(3) or Cr(2)–Cr(3) (2.647 (7) vs. 2.552 (6) and 2.565 (8) Å, respectively). The Cr–S($\mu_3$) distances also reflect this distortion with Cr(1)–S(1) and Cr(2)–S(1) longer than Cr(3)–S(1) (2.323 (8) and 2.421 (11) vs. 2.208 (9) Å, respectively). The S(2) atom is more symmetrically displaced and in this case the distortion brings it closer to Cr(1) and Cr(2) and away from Cr(3) (Cr(1)–S(2) = 2.309 (9), Cr(2)–S(2) = 2.325 (13), Cr(3)–S(2) = 2.340 (13) Å). The Cr–S($\mu_2$) distances also fall into two distinct regions Cr(1)–S(3) and Cr(2)–S(3) (2.429 Å, av) and are both notably longer than the other Cr–$\mu_2$-S bond lengths (2.340 Å, av). All of these distances are in the normally observed ranges for Cr–S bonds (ca. 2.2–2.4 Å).[4]

The Cr–P distances also fall within two distinct ranges. Those to Cr(1) and Cr(2) are noticably shorter (2.292 (12)–2.393 (9) Å) than those to Cr(3) (2.435 (14) and 2.454 (10) Å).

The coordination geometry about each Cr atom is roughly octahedral. Thus typical trans angles subtended at Cr(1) S(3)–Cr(1)–S(5), S(1)–Cr(1)–P(1), and S(2)–Cr(1)–P(2) are 173.3 (4)°, 170.0 (4)°, and 171.4 (4)°, respectively. The cis angles P(1)–Cr(1)–P(2), S(1)–Cr(1)–P(2), and S(2)–Cr(1)–S(1) are 82.1 (3)°, 88.3 (3)°, and 100.1 (3)°, respectively.

Regarding each S atom as a dianion gives eight d electrons for **1**. Extended Hückel calculations[11] were carried out on a model compound, $Cr_3S_5(PH_3)_6$, at $D_{3h}$ symmetry where all bond lengths and angles have been averaged from the experimental structure for **1**. The valence, metal-centered orbitals are shown from a top view in Figure 2. The lowest three orbitals, $a_1'$ and $e'$, are $\sigma$-bonding. At higher energy the $a_1''$ is $\pi$ antibonding and $e''$ is $\pi$ bonding. The $a_1''$ level lies at a lower energy than $e''$ because one combination of lone pairs on the $\mu_2$-S atoms has a large overlap with $e''$ and destabilizes it. There is no S combination that matches the symmetry of $a_1''$. Calculations[12] on $Mo_3S_2Cl_9^{3-}$, an isoelectronic molecule, give the same level pattern and relative energies except that $e''$ lies slightly lower in energy than $a_1''$. The $\mu_2$-Cl lone pairs are much weaker $\pi$ donors than S. A first-order Jahn–Teller distortion occurs in this complex giving two long and one short Mo–Mo bond lengths.[13] In our system the 0.62-eV energy gap between the HOMO and LUMO is relatively small and signals a possible second-order Jahn–Teller distortion. Allowing the Cr(1)–Cr(2) distance to increase while the Cr(1)–Cr(3) and Cr(2)–Cr(3) bonds contract reduces the molecular symmetry to $C_{2v}$. The A component of $e''$ mixes into $a_1''$ with the phases shown in Figure 2 to increase the $\pi$ bonding between Cr(1) and Cr(3) along with Cr(2) and Cr(3). This stabilizes $a_1''$ and provides an electronic rationale for the distortion observed in **1**.

Further studies on phosphine-stabilized sulfido clusters of the transition metals are in progress.

**Acknowledgments.** We thank the National Science Foundation (CHE 82-11883), the Robert A Welch Foundation (F-816 and E-705), The Research Corporation, The Tescar Advanced Technology Research Program (TATRP), and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support. R.A.J. thanks the Alfred P. Sloan Foundation for a research fellowship (1985–87).

**Registry No. 1**, 100681-53-6.

**Supplementary Material Available:** Complete listing of bond lengths, angles, atomic coordinates, thermal parameters, and structure factors (22 pages). Ordering information is given on any current masthead page.

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[8] Full experimental details will be published separately. Yield 20%, **1** crystallizes from toluene (−20 °C) as black prisms; mp >360 °C, IR (KBr disk) 2934 (m), 2897 (s), 1410 (s), 1290 (m), 1271 (s), 1262 (s), 1095 (br, m), 1022 (br, m), 984 (w), 943 (s), 927 (s), 891 (m), 801 (m), 739 (w), 707 (m), 670 (w), 645 (m), 411 (m), 400 (m), 307 (w), 250 (m), 226 (s) cm$^{-1}$. $^1$H NMR (90 MHz in $Me_2SO$-$d_6$) $\delta$ 1.40 m, 36 H, $CH_3$; $\delta$ 1.69 m, 12 H, $CH_2$. $^{31}P\{^1H\}$ (In $Me_2SO$-$d_6$ at 32.34 MHz), $\delta$ 48.83 (relative 85% $H_3PO_4$ (aq), $\delta$ 0.0). Microanal. Calcd C, 28.20%; H, 6.31%; P, 24.24%. Found: C, 28.12%; H, 6.40%; P, 23.56%. There is no IR spectroscopic evidence for the presence of S–H and the complex is EPR silent at room temperature and at −196 °C in toluene. The effective magnetic moment at room temperature $\mu_{eff} = 0.0$ $\mu_B$. (Evans method, toluene). These data and the sharpness of the $^{31}$P NMR signal rule out the possibility of a paramagnetic Cr(III)(III)(III) formulation for **1**.

[9] CAD-4, the crystal data: $C_{18}H_{48}Cr_3P_6S_5$; $M_r = 766.74$, orthorhombic, $Pna2_1$ (No. 33), $a = 20.754$ (3) Å, $b = 9.103$ (7) Å, $c = 18.443$ (4) Å, $U = 3484.3$ (5) Å$^3$, $D_c = 1.462$ g cm$^{-3}$, $Z = 4$, (Mo K$\alpha$) = 0.71073 Å (graphite monochromator), $\mu = 14.68$ cm$^{-1}$. Methods: MULTAN, difference Fourier, full-matrix least squares. Refinement of 1483 unique observed reflections ($I > 3\sigma I$) out of 1584 measured ($2° < 2\theta < 50°$), gives current $R$ and $R_w$ values of 0.072 and 0.080, respectively. All non-hydrogen atoms were refined anisotropically, H atoms were not located. The largest peak in the final difference Fourier was 0.8 e Å$^{-3}$.

[10] Deviations (Å) from the least-squares plane through Cr(1), Cr(2), Cr(3), S(3), S(4), and S(5) are Cr(1) −0.003 (4), Cr(2) 0.025 (6), Cr(3) −0.011 (4), S(3) −0.010 (11), S(4) −0.008 (8), S(5) 0.007 (10), and S(1) −1.764 (7), S(2) 1.784 (7). A complete listing of all bond lengths and angles is available. See paragraph at end of paper regarding supplementary material.

[11] Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686. The parameters for the calculations may be found in: Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801 and ref 12.

[12] Jiang, Y.; Tang, A.; Hoffmann, R.; Huang, J.; Lu, J. *Organometallics* **1985**, *4*, 27.

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# Metal–Metal Double-Bond Formation and Control of Cluster Geometry via Steric Design: Syntheses and Structures of the First $Ir_4$ Arsenido and Phosphido Complexes: Planar Unsaturated $[Ir(\mu\text{-}t\text{-}Bu_2As)]_4(\mu\text{-}CO)_2(CO)_2(Ir{=}Ir)$ and Tetrahedral Saturated $[Ir(\mu\text{-}Cy_2P)CO]_4(\mu\text{-}CO)_2$ (Cy = Cyclohexyl)

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We have previously shown that the use of bulky bridging phosphido ($R_2P^-$) or arsenido ($R_2As^-$) ligands can dramatically alter the stoichiometries, structures, and reactivites of their d-block transition-metal complexes.[2] We describe here the synthesis, structures, and characterization of $[Ir(\mu\text{-}t\text{-}Bu_2As)]_4(CO)_2(\mu\text{-}CO)_2$ (**1**) and $[Ir(\mu\text{-}Cy_2P)(CO)]_4(\mu\text{-}CO)_2$ (**3**), which, to our knowledge are the first tetranuclear Ir arsenido and phosphido stabilized clusters to be reported (Scheme I)[3,4].

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[1] Alfred P. Sloan Foundation Fellow, 1985–1987.

[2] See, for example: Gaudiello, J. G.; Wright, T. C.; Jones, R. A.; Bard A. J. *J. Am. Chem. Soc.* **1985**, *107*, 888. Kang, S.-K.; Albright, T. A.; Jones, R. A.; Wright, T. C. *Organometallics* **1985**, *4*, 666. Jones, R. A.; Wright, T. C. *Organometallics* **1983** *2*, 1842. Jones, R. A.; Lasch, J. G.;Norman N. C.; Whittlesey, B. R.; Wright, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 6184.

[3] Few other Ir phosphido species are known. $Ir(COD)(\mu\text{-}pz)(\mu\text{-}Ph_2P)_2Ir(C_8H_{13})$ (pzH = pyrazole; COD = 1,5-cyclooctadiene): Bushnell, G. W.; Stobart, S. R.; Vefghi, R.; Zaworotko, M. J. *J. Chem., Soc. Chem. Commun.* **1984**, 282. See also, for $Ir_3(\mu\text{-}PPh)(CO)_6(Ph)(dppm)$: Harding, M. M.; Nicholls, B. S.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1983**, 1479. For the phosphinidene complex $Ir_4(\mu_3\text{-}PhP)(\mu_2\text{-}CO)_3(PPh_3)_4$: Demartin, F.; Manassero, M.; Sansoni, M.; Giarlaschelli, L.; Sartorelli, U. *J. Organomet. Chem.* **1981**, *204*, C10.

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