

Scheme I

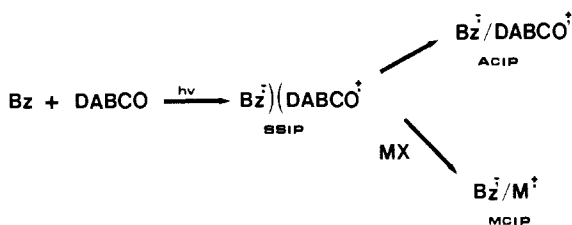


Table I. Heats of Reaction of the Photoreduction of Benzophenone by DABCO^a

solvent	added salt	ΔH_r , ^b kcal/mol
acetonitrile	none	52.0
	LiClO ₄	46.7
	NaClO ₄	47.7
	(<i>n</i> -Bu) ₄ NClO 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, ΔH_r is the enthalpy difference between the corresponding ion pair and initial reactants.

ΔH_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 ΔH_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 ΔH_r in ethanol.¹¹

The energies of the ion pairs in acetonitrile are ordered, $E(\text{Li}^+) < E(\text{Na}^+) < E((n\text{-Bu})_4\text{N}^+) \approx E(\text{no salt})$, 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*-Bu)₄NClO₄ 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, ΔG , 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, ϵ 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

(9) The volume change for a photochemical reaction, ΔV , may contribute to the observed acoustic wave. In this case, the negative ΔV of reaction would give a seemingly large value for ΔH_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*-Bu)₄ClO₄ 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 TBABF₄ in CH₃CN, vs. Ag/AgNO₃ (0.1 M), TBABF₄ (0.5 M). Sweep rate from 50 to 1 V/s.

accord with literature values.¹⁴ By use of this difference, $\epsilon = 37.5$ ¹⁵ and $r = 2.9$ Å,¹⁶ the above equation gives $\Delta G \approx 54$ 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 $\Delta G \approx 50$ kcal/mol which agrees well with the experimental value.¹⁹

The reasonable agreement between the calculated and experimental values suggests that the term $e^2/(\epsilon r)$ is small and, in particular, that ϵ 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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Mixed Valence, Phosphine Stabilized Sulfido Clusters of the Transition Metals: Synthesis and Structure of Cr₃(μ_3 -S)₂(μ_2 -S)₃(dmpe)₃, Cr(III,III,IV) (dmpe = Bis(1,2-dimethylphosphino)ethane). A Structurally Characterized Cr₃ Cluster

Atta M. Arif, John G. Hefner, and Richard A. Jones*

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

Thomas A. Albright* and Sung-Kwon Kang

Department of Chemistry, The University of Houston Houston, Texas 77004

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The relevance of complexes containing transition-metal-sulfur bonds to biological systems¹ as well as to industrially important

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reactions² 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 Cr₃(μ₃-S)₂(μ₂-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 Cr₃ 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

The reaction of anhydrous CrCl₂ with NaSH (1:2) in methanol at –78 °C gives an immediate black suspension. Addition of excess

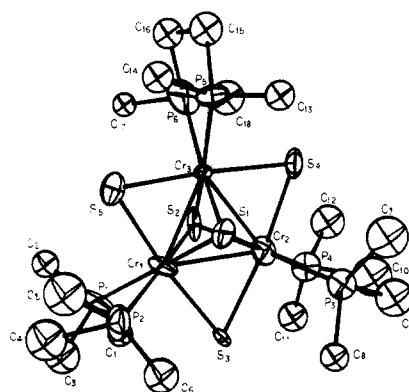


Figure 1. ORTEP view of **1**. Key bond lengths and angles are noted in the text.

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(3) Recent examples: sulfido clusters with phosphine ligands; [Ni₃(μ₃-X)₂(PR₃)₆]²⁺ (R = Me, X = S; R = Et, X = S, Se) and [Ni₃(μ₄-S)₃(μ₃-S)₆(PEt₃)₆]²⁺ (Ceccconi, F.; Ghilardi, C. A.; Midollini, S. *Inorg. Chem.* **1983**, *22*, 3802) [Co₆(μ₃-S)₈(PEt₃)₆]BPh₄ (Ceccconi, F.; Ghilardi, C. A.; Midollini, S. *Inorg. Chim. Acta. Lett.* **1982**, *64*, L47. See also, for Zr₃(S)(t-BuS)₁₀ Coucouvanis, D.; Hadjikyriacou, A.; Kanatzidis, M. G. *J. Chem. Soc., Chem. Commun.* **1985**, 1224. For the linear Cr(III) trimer (PPh₄)₂Na[Cr₃(SCH₂CH₂O)₃]; Nicholson, J. R.; Wang, R. J.; Huffman, J. C.; Christou, G.; Chang, H. R.; Hendrickson, D. N. *J. Chem. Soc., Chem. Commun.* **1985**, 1781.

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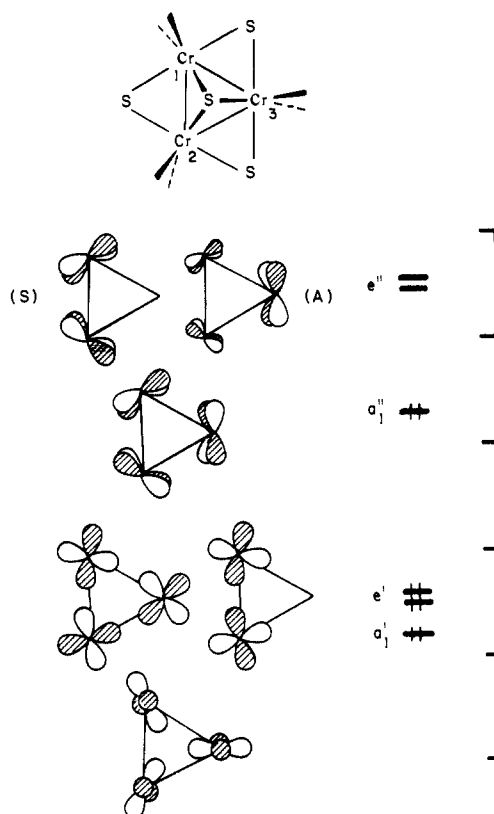


Figure 2. Top view of the valence, metal-centered orbitals in Cr₃S₃(PH₃)₆ at a D_{3h} geometry. The energy scale on the right side of this figure is divided into 0.5-eV intervals.

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, Me₂SO, and MeOH. It is insoluble in hexane and appears to decompose in CH₂Cl₂. It appears to be air stable in the solid state and also in solution, at least for several hours. NMR data (¹H and ³¹P) for **1** show only the presence of coordinated dmpe (³¹P{¹H} δ 48.83 s, free dmpe, δ –46.10).⁸

(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 Pna_2 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 μ_3 -S atom with three edge bridging μ_2 -S atoms. The $Cr(\mu_2-S)_3$ core is virtually planar¹⁰ while the two μ_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(μ_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(μ_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– μ_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 noticeably 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 calculations¹¹ 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 σ -bonding. At higher energy the a_1'' is π antibonding and e'' is π bonding. The a_1'' level lies at a lower energy than e'' because one combination of lone pairs on the μ_2 -S atoms has a large overlap

with e'' and destabilizes it. There is no S combination that matches the symmetry of a_1'' . Calculations¹² 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 μ_2 -Cl lone pairs are much weaker π 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 π 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.

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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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(13) Huang, J.; Shang, M.; Lui, S.; Lu, J. *Sci. Sin. (Engl. Ed.)* **1982**, *25*, 1270.

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 $[Ir(\mu-t-Bu_2As)]_4(\mu-CO)_2(CO)_2(Ir=Ir)$ and Tetrahedral Saturated $[Ir(\mu-Cy_2P)CO]_4(\mu-CO)_2$ (Cy = Cyclohexyl)

Atta M. Arif, Richard A. Jones,*¹ Stuart T. Schwab, and Bruce R. Whittlesey

Department of Chemistry
The University of Texas at Austin
Austin, Texas 78712

Received November 21, 1985

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 reactivities of their d-block transition-metal complexes.² We describe here the synthesis, structures, and characterization of $[Ir(\mu-t-Bu_2As)]_4(CO)_2(\mu-CO)_2$ (**1**) and $[Ir(\mu-Cy_2P)CO]_4(\mu-CO)_2$ (**3**), which, to our knowledge are the first tetranuclear Ir arsenido and phosphido stabilized clusters to be reported (Scheme I)^{3,4}.

(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. $Ir(COD)(\mu-pz)(\mu-Ph_2P)_2Ir(C_6H_5)_3$ (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 $Ir_3(\mu-PPh)(CO)_6(Ph)(dppm)$: Harding, M. M.; Nicholls, B. S.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1983**, 1479. For the phosphinidene complex $Ir_4(\mu_3-PhP)(\mu_2-CO)_3(PPh_3)_4$: Demartin, F.; Manassero, M.; Sansoni, M.; Giarlascelli, L.; Sartorelli, U. *J. Organomet. Chem.* **1981**, *204*, C10.

(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} . ¹H NMR (90 MHz in Me_2SO-d_6) δ 1.40 m, 36 H, CH_3 ; δ 1.69 m, 12 H, CH_2 . ³¹P{¹H} (in Me_2SO-d_6 at 32.34 MHz), δ 48.83 (relative 85% H_3PO_4 (aq), δ 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 ³¹P 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, Pna_2 (No. 33), $a = 20.754$ (3) Å, $b = 9.103$ (7) Å, $c = 18.443$ (4) Å, $U = 3484.3$ (5) Å³, $D_c = 1.462$ g cm^{-3} , $Z = 4$, ($Mo K\alpha$) = 0.710 73 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 ($2^\circ < 2\theta < 50^\circ$), 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 $e \text{ \AA}^{-3}$.

(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.; Thibault, 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.; Thibault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801 and ref 12.