complexes (where $n = 0$–4) containing a bonded tetrahedral-like X_nM_{4-n} cluster fragment are as follows: (1) X_4 molecules of T_d symmetry, *e.g.*, white P_4 and yellow As_4; (2) $X_3M(CO)_3$ molecules of C_{3v} symmetry, none known before $As_3Co(CO)_3$;[14] (3) $X_2M_2(CO)_6$ molecules of C_{2v} symmetry, *e.g.*, $S_2Fe_2(CO)_6$[15] and $As_2Co_2(CO)_6$;[3,4] (4) $XM_3(CO)_9$ molecules of localized C_{3v} symmetry, *e.g.*, $SCo_3(CO)_9$,[7] $SeCo_3(CO)_9$,[9] and $RCCo_3(CO)_9$ (where R represents CH_3,[16] $C(O)CCo_3(CO)_9$,[17] $OBH_2N(C_2H_5)_3$,[18] $C_2HCo_2(CO)_6$,[19] and $C_3Co_3(CO)_9$[19]); (5) $M_4(CO)_{12}$ molecules of T_d symmetry, *e.g.*, $Ir_4(CO)_{12}$.[20–23]

Further characterization of $As_3Co(CO)_3$ by chemical and physical means (including redox reactions) is in progress to assess the chemical versatility of this complex.

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Organometallic Pnicogen Complexes. IV. Synthesis, Structure, and Bonding of New Organometallic Arsenic–Metal Atom Clusters Containing a Metal-Bridged Multiply Bonded As_2 Ligand: $Co_2(CO)_6As_2$ and $Co_2\{(CO)_5P(C_6H_5)_3\}As_2$[1,2]

Sir:

Despite intensive research activity concerning (transition metal)–N_2 complexes,[3] there have been no previously known examples of (transition metal)–X_2 complexes for the other group Va family elements (X = P, As, Sb, Bi) even though vapor pressure and spectroscopic studies[4] demonstrate the existence at high temperatures of diatomic X_2 molecules for these congener elements in the gaseous state. This paper reports the preparation and structural characterization of two dicobalt–As_2 complexes, $Co_2(CO)_6As_2$ and a derivative $Co_2\{(CO)_5P(C_6H_5)_3\}As_2$, which display *tetrahedral* M_2X_2 geometry rather than the *linear* M–X–X–M geometry recently established from Raman spectral studies[5] for the diruthenium–N_2 fragment in the bridging nitrogen $\{[Ru(NH_3)_5]_2N_2\}^{4+}$ cation.[5,6] The molecular compound $Co_2\{(CO)_5P(C_6H_5)_3\}As_2$ has been found from an X-ray crystallographic analysis to contain the shortest known As–As bond length reported to date; the exceptionally short As–As distance has been interpreted from MO considerations in terms of a high degree of As–As multiple-bond character being present in the tetrahedral Co_2As_2 system.

$Co_2(CO)_6As_2$ is a red liquid (mp $\sim -10°$) produced by the reaction of $Co_2(CO)_8$ with excess $AsCl_3$ in THF and purified by chromatography on silica gel. Its mass spectrum shows the presence of all the possible $As_2Co_2(CO)_n^+$ ions ($n = 0$–6) with the most prominent species being the parent ion and the bare $As_2Co_2^+$ cluster. The molecular architecture of $Co_2(CO)_6As_2$ was established from an X-ray crystallographic analysis of the monosubstituted triphenylphosphine derivative, $Co_2\{(CO)_5P(C_6H_5)_3\}As_2$ (*vide infra*), which showed that the unsubstituted $Co_2(CO)_6As_2$ molecule must be structurally analogous to the electronically equivalent $Fe_2(CO)_6X_2$ molecules (X = S, Se).[7] The molecular configuration of $Fe_2(CO)_6S_2$ (Figure 1)[8] ideally possesses C_{2v}-2mm symmetry in the solid state; dipole moment and infrared spectral analysis[9] show its over-all molecular geometry to remain unchanged on dissolution. The close similarity of the infrared solution spectrum[10] of $Co_2(CO)_6As_2$ with that of $Fe_2(CO)_6S_2$ allows the gross $Co_2(CO)_6As_2$ geometry to be assigned with certainty as the C_{2v} $Fe(CO)_6S_2$-type structure.

In order to obtain a solid derivative $Co_2(CO)_6As_2$ suitable for X-ray examination, $Co_2(CO)_6As_2$ was refluxed in benzene with excess triphenylphosphine which afforded red $Co_2\{(CO)_5P(C_6H_5)_3\}As_2$. This latter compound crystallizes in the triclinic system with two molecules in a unit cell of symmetry $P\bar{1}$ and of dimensions $a = 11.391 \pm 0.008$ Å, $b = 13.033 \pm 0.009$ Å, $c = 9.120 \pm 0.007$ Å, $\alpha = 108.17 \pm 0.02°$, $\beta = 103.84 \pm 0.01°$, $\gamma = 74.22 \pm 0.02°$; $\rho_{calcd} = 2.02$ g cm^{-3} *vs.* $\rho_{obsd} = 1.97 \pm 0.06$ g cm^{-3} (flotation method). Three-dimensional intensity data were collected with Mo Kα radiation on a General Electric four-angle automated diffractometer.

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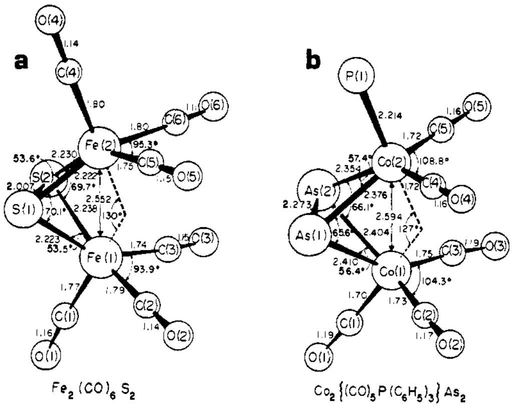

Figure 1. The geometries of (a) the $Fe_2(CO)_6S_2$ molecule and (b) the $Co_2\{(CO)_5P\}As_2$ fragment of the $Co_2\{(CO)_5P(C_6H_5)_3\}As_2$ molecule (*i.e.*, for clarity the three phosphorus-attached phenyl groups were omitted). The $Co_2\{(CO)_5P\}As_2$ fragment ideally possesses C_s-m symmetry, while $Fe_2(CO)_6S_2$ approximately conforms to C_{2v}-2mm symmetry. The over-all molecular configuration of the unsubstituted $Co_2(CO)_6As_2$ molecule is shown (see text) to be analogous to that of the $Fe_2(CO)_6S_2$ molecule.

The structure was determined from Patterson and Fourier maps and refined by full-matrix least squares to a conventional R value of 7.2% based on 1911 independent observations with $|F_o| > 4\sigma(F_o)$.

Figure 1 compares the important bond lengths and angles of the $Co_2\{(CO)_5P(C_6H_5)_3\}As_2$ and $Fe_2(CO)_6S_2$ molecules. These two molecules and $As_2Co_2(CO)_6$ are structurally and electronically related to the acetylene-bridged $Co_2(CO)_6(C_6H_5C_2C_6H_5)$ molecule.[11-13] The $As_2Co_2(CO)_6$ molecule also is homologously related to the electronically equivalent As_4 and $As_3Co(CO)_3$ molecules[1] as a dimetal derivative of As_4 in which two arsenic atoms have been replaced by two $Co(CO)_3$ groups.

A prime stereochemical feature is that the As–As bond length of only 2.273 (3) Å in the triphenylphosphine derivative of $As_2Co_2(CO)_6$ is 0.10 Å less than that of 2.372 (5) Å in $As_3Co(CO)_3$[1] which in turn is 0.06–0.09 Å less than the average bond lengths found in gaseous As_4 (2.44 Å),[14] $[AsCH_3]_5$ (2.428 (8) Å),[15] and $[AsC_6H_5]_6$ (2.456 (5) Å).[16] This significant As–As bond-shortening trend on substitution of $Co(CO)_3$ groups in place of arsenic atoms in As_4 may be rationalized from the premise that the more electronegative $Co(CO)_3$ system effectively functions as an "electron sink" which by a resultant partial charge transfer from the arsenic to the $Co(CO)_3$ system decreases the antibonding orbital character between the arsenic atoms. A delocalized MO model incorporating this viewpoint was utilized[1] to explain the exceptional stability of the $As_3Co(CO)_3$ molecule relative to the As_4 molecule. A σ–π MO formulation similar to the one employed by Brown[13] to describe the dimetal–acetylene interaction in $Co_2(CO)_6(C_6H_5C_2C_6H_5)$ has been invoked in the bonding representations of $Co_2(CO)_6As_2$ and the triphenylphosphine analog in order to account conveniently for the large As–As multiple-bond character in accord with the extremely short As–As bond length in $Co_2\{(CO)_5P(C_6H_5)_3\}As_2$. The same symmetry classification of orbitals utilized by Brown[13] in $Co_2(CO)_6(C_6H_5C_2C_6H_5)$[17-20] is applicable except that one instead must consider the relative importance of the 3d, 4s, 4p, and 4d valence atomic orbitals of the arsenic atoms to the symmetry-allowed $Co–As_2–Co$ molecular orbitals.

A prominent stereochemical difference between $Co_2\{(CO)_5P(C_6H_5)_3\}As_2$ and $Fe_2(CO)_6S_2$ which clearly accents an important bonding trend in these $M_2(CO)_6X_2$ molecules is revealed from a comparison of the X–X bond lengths in these two molecules. The As–As bond length in $Co_2\{(CO)_5P(C_6H_5)_3\}As_2$ is 0.16–0.18 Å shorter than As–As single-bond lengths, whereas the S–S bond length of 2.007 (5) Å in $Fe_2(CO)_6S_2$ is close to the S–S bond lengths of range 2.01–2.10 Å found[21-26] in a large number of disulfide compounds. This bond-length evidence for a considerably greater π-bond order in the As–As bond of $Co_2\{(CO)_5P(C_6H_5)_3\}As_2$ compared to that in the S–S bond of $Fe_2(CO)_6S_2$ indicates that the two antibonding π^* orbitals of the As_2 fragment in the Co_2As_2 complex are populated with significantly less charge than the corresponding π^* orbitals of the S_2 fragment in the Fe_2S_2 complex. This is not unexpected in that As_2 as a neutral free entity (like acetylene) would possess a triple bond while neutral S_2 (like O_2) is considered to have a double bond. Unlike disulfide systems[26] no (bond length)–(valence-bond order) curve exists for the As–As systems. Nevertheless, based on the bridging acetylene C–C bond length of 1.37 Å[13] in $Co_2(CO)_6(C_6H_5C_2C_6H_5)$ being near the normal C–C double-bond length value of 1.33 Å and the single-to-double bond length range being 1.9–2.1 Å for the S–S systems,[26] it is presumed that the As–As distance in $Co_2\{(CO)_5P(C_6H_5)_3\}As_2$ roughly corresponds to a double-bond length. This indicates that there is an appreciable for-

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ward-bonding–back-bonding Co–As_2–Co interaction which concomitantly results in a decrease of the As–As valence-bond order from *three* (as a neutral species) to approximately *two*. Similar considerations of the corresponding synergic bonding mechanism in $Fe_2(CO)_6S_2$ suggest a resultant S–S total valence-bond order decrease from *two* (as neutral free S_2) to a value near *one* in this Fe_2S_2 complex.[26] Further synthetic and structural work is in progress to appraise and amplify these bonding conclusions.

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Trifluoroacetolysis of Simple Primary Alkyl Toluenesulfonates[1]

Sir:

In earlier work, EtOH, AcOH, and HCOOH proved to be instructive and useful solvents in probing the competition between anchimerically assisted ionization (k_Δ) and anchimerically unassisted ionization (k_s) in solvolysis of simple alkyl systems.[2,3] The solvent sequence of k_Δ/k_s ratios in solvolysis of marginal systems, such as 2-phenyl-1-ethyl,[2b,c] is EtOH < AcOH < HCOOH. With the simplest primary alkyl toluenesulfonates,[3a] the observed MeOTs–EtOTs–*i*-BuOTs–neopentyl-OTs (neoPenOTs) sequence of solvolysis rates at 75° changed from a steeply descending one, 4000:1750:80:1, in EtOH to 10:9:2.8:1 in AcOH, and finally to the relatively flat sequence, 0.56:1.0:1.22:1.0, in HCOOH. Formolysis of MeOTs and EtOTs was judged to be far from the Lim. category; in other words, it occurs with substantial nucleophilic solvent participation.

The formolysis rate of neoPenOTs, just as high as that of EtOTs in spite of the very large steric hindrance to backside solvent entry, was most simply explained as due to anchimeric assistance from carbon participation.[3a] In the case of *i*-BuOTs, the formolysis rate was judged to be consistent with at least some successful competition with k_s from k_Δ due to hydrogen participation.[3a] Since our earlier remarks regarding neopentyl solvolysis, various other discussions[4] have appeared pro and con with the idea of anchimeric assistance to neopentyl ionization.

Quite recently, CF_3COOH, with its very low nucleophilicity and relatively high ionizing power, has become recognized as an important solvolyzing solvent which gives rise to k_Δ/k_s ratios much higher than in HCOOH.[5] We have found this solvent to be very instructive in the case of the simplest primary alkyl systems, and in this communication we report the trifluoroacetolysis of the Me, Et, *n*-Pr, *i*-Bu, and neoPen series of *p*-toluenesulfonates.

The solvolyses in CF_3COOH were followed using the absorption of the alkyl tosylate at 273 mμ.[6] The first-order solvolysis rate constants (k_t) listed in Table I were measured in the absence of CF_3COONa. In the case of MeOTs, EtOTs, and *n*-PrOTs, k_t increases substantially on addition of CF_3COONa. The increase in k_t at 100° can be fit with second-order rate constants equal to 6.1×10^{-5}, 4.9×10^{-5}, and 4.2×10^{-5} M^{-1} sec^{-1}, for MeOTs, EtOTs, and *n*-PrOTs, respectively. For *i*-BuOTs and neoPenOTs, no sensitivity of k_t to CF_3COONa addition was detected.

The products of reaction were followed by nmr. MeOTs and EtOTs produce the corresponding $ROCOCF_3$ quantitatively. No deuterium scrambling (<2%) was observed when β-d_3-EtOTs was solvolyzed. Propyl tosylate produces 11.4% *n*-$PrOCOCF_3$ plus 88.6% *i*-$PrOCOCF_3$ at 100° and 10.3% *n*-$PrOCOCF_3$ plus 89.7% *i*-$PrOCOCF_3$ at 125°. The solvolysis of 2,2-d_2-1-PrOTs at 100° yields 83.7% *i*-$PrOCOCF_3$ containing <0.05 α proton (δ 4.75, based on CH_2Cl_2 at δ 5.30) and 5.03 β protons (δ 1.03). Thus, the *i*-$PrOCOCF_3$ does not arise from solvent addition to propene[7] and there is no extensive equilibration of the protons. The remaining 16.3% product is *n*-$PrOCOCF_3$. In the solvolysis of 1,1-d_2-1-PrOTs no α proton signals were evident (<0.05 proton) in the residual *n*-PrOTs or the *n*-$PrOCOCF_3$ product. Thus, the solvolysis is not appreciably accompanied by 1,3-hydride shifts[8] or formation and reopening of cyclopropane.[9] The solvolysis of *i*-BuOTs yields only a rearranged product, this being mainly *t*-$BuOCOCF_3$ accompanied by as much as 20% 2-$BuOCOCF_3$. Quantitative product analysis is difficult in this case since the product is unstable even in the presence of CF_3COONa. *t*-$AmOCOCF_3$ is produced quantitatively from neoPenOTs.

As seen in Table I the relative rates in CF_3COOH at 75.0° show a steeply rising trend for the primary tosylates, the MeOTs–EtOTs–*n*-PrOTs–*i*-BuOTs–neoPenOTs sequence being 1:13:93:3060:5970, in sharp contrast to the sequences previously observed[3a] in EtOH, AcOH,

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[1] Research sponsored by the National Science Foundation.

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