Cation–Anion Interplay and Crystal Construction in Organometallic Salts of Large Cluster Anions

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Received July 30, 1991

The organization of cations and anions in the crystalline salts of transition-metal carbonyl cluster anions of nuclearity six and ten has been investigated by means of approximate atom–atom potential energy calculations and computer graphics. It has been shown that large carbonyl anions establish intermolecular interactions that closely resemble those observed in molecular crystals of neutral species. A clear tendence to form anion piles surrounded by cation belts has been observed. The structure of the anionic piles depends on the size of the cation and on the actual free charge. Preferential anion–cation pairing has been observed only in the $[(PhCH_2)Me_3N]^+$ and $[Ph_4P]^+$ salts of the dianion $[Rh_6C(CO)_{15}]^{2-}$.

Introduction

Most high-nuclearity transition-metal carbonyl clusters are ions;[1] hence, a large portion of the structural characterization by diffraction methods in this field is carried out on salts. These crystalline materials have been named "soft salts" to account for the large size of the component ions compared with that of the particles forming simple solid salts.[2] That "large cations are stabilized by large anions" was recognized long ago by Basolo.[3] He pointed out that this empirical relationship could be effectively exploited to isolate metal complexes in the form of stable crystalline salts. Such a simple rule has been applied (without much awareness, perhaps) by cluster chemists over the past three decades to isolate and characterize an enormous number of new species. However, no systematic study of the effect of the counterion choice on the crystallization process has ever been carried out, the crystallization of new species (and the consequent structural characterization) being usually based on the "first come (crystallized) first served (put on a diffractometer)" principle.

In spite of early indications[4] that metal clusters would provide valuable model systems for chemisorption on metal surfaces and a bridge between molecular and solid-state chemistry, the solid-state properties of these materials have not been given much attention. Research in this area of organometallic chemistry has only recently begun. For example, the multiple-redox properties of solid cubanelike clusters have been studied,[2] while correlations between crystalline structures and phase-transition phenomena have been used to study thermochromic materials.[5] EPR measurements and studies of the magnetic behavior of high-nuclearity clusters of various metals (Os, Pt, Pd, Au, etc.)[6] have also afforded the first fascinating indications that metal clusters in the solid state can show properties that are neither those of bulk metals nor those of dispersed metals.[7]

In previous papers[8-12] we have investigated the relationship between the structure of neutral organometallic molecules and the structure of their crystals. This approach has been fundamental in the appreciation of the differences between the *collective* molecular properties of the crystalline assemblage and the properties of the *individual* molecular entity replicated by space-group and translation symmetry within the lattice. We have been able to tackle various aspects of the (rather unexplored) solid-state organometallic chemistry field such as the effect of intermolecular (packing) forces on the molecular structure and dynamic behavior shown by neutral binary carbonyls in the solid state[8,9] and the occurrence of reorientational phenomena in mononuclear and polynuclear organometallic complexes.[10] The molecular organization in crystalline arenes and in mononuclear arene complexes, and the presence of well-defined and recurring packing motives in metal carbonyls and in carbonyl–arene clusters, have also been investigated.[11]

Further, new insights into the bonding in $Co_2(CO)_8$ have been gained, leading to the discovery of a channeled crystal lattice which offers possibilities for diffusion and reactivity in the solid state.[12] This has all been achieved essentially by expanding our way of looking at the result of a diffraction experiment, from the single molecule "denuded" of its crystalline environment to the entire molecular ensemble constituting the crystalline material.

In an attempt to broaden this perspective further, we now wish to extend this approach to the study of *ionic* carbonyl clusters. Our aim is to answer the following questions:

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Table I. Crystalline Deca- and Hexametallic Cluster Salts[a]

species (ref)	space group	*a*, Å (*α*, deg)	*b*, Å (*β*, deg)	*c*, Å (*γ*, deg)
$[Os_{10}C(CO)_{24}][PPN]_2$[b] (13)	$P\bar{1}$	27.157 (5) (96.37 (2))	17.535 (4) (100.71 (2))	**10.470** (2) (85.92 (2))
$[H_4Os_{10}(CO)_{24}][PPN]_2$ (14)	$P\bar{1}$	26.940 (3) (96.17 (1))	17.421 (2) (100.68 (1))	**10.601** (2) (86.47 (1))
$[Ru_{10}C(CO)_{24}][PPN]_2$ (15)	$P\bar{1}$	17.520 (5) (100.61 (3))	27.102 (9) (96.28 (3))	**10.444** (2) (85.74 (6))
$[Os_{10}C(CO)_{22}(NO)I][PPN]_2$ (16)	$P\bar{1}$	27.366 (3) (96.57 (2))	17.569 (3) (100.39 (3))	**10.459** (2) (85.74 (2))
$[H_2Os_{10}C(CO)_{24}]$ (17)	$C2/c$	21.479 (6)	**9.890** (3) (120.42 (2))	20.807 (4)
$[HOs_{10}C(CO)_{24}][Ph_3MeP]$ (18)	$P\bar{1}$	16.211 (85.30)	15.052 (96.38)	**12.016** (111.43)
$[HOs_{10}C(CO)_{24}][Ph_4As]$ (18)	$P6_3mc$	16.660	16.660	**12.070**
$[Co_6C(CO)_{15}][Et_4N]_2$ (19)	$P2_1/n$	**8.890** (2)	22.790 (10) (96.00 (1))	20.545 (6)
$[Rh_6C(CO)_{15}][Ph_4P]_2$ (19)	$P\bar{1}$	14.784 (8) (96.50 (5))	18.796 (13) (90.78 (5))	**11.339** (7) (86.35 (5))
$[Co_6N(CO)_{15}][PPN]$ (20)	$P\bar{1}$	19.686 (8) (95.69 (6))	**9.065** (5) (69.99 (6))	15.737 (7) (88.31 (6))
$[Rh_6N(CO)_{15}][PPN]$ (21)	$P\bar{1}$	19.841 (5) (95.88 (3))	**9.156** (3) (70.12 (3))	16.066 (5) (87.99 (3))
$[Co_6C(CO)_{15}][(PhCH_2)Me_3N]_2$[c] (22)	$C2/c$	21.752 (2)	11.350 (1) (112.28 (1))	18.099 (2)
$[Rh_6C(CO)_{15}][(PhCH_2)Me_3N]_2$[c] (23)	$C2/c$	22.17 (2)	11.46 (1) (112.72 (6))	18.51 (2)

[a] Bold cell axes = interanion or intermolecular (in the case of $[H_2Os_{10}C(CO)_{24}]$) separations between cluster centers in the lattice (see text). [b] PPN = $[(Ph_3P)_2N]^+$. [c] The separation between next-neighboring anions does not correspond to a unit cell translation (the shortest distance between cluster centers is 10.530 Å for M = Rh).

(i) Do crystalline salts of high-nuclearity carbonyl cluster anions conform to the same close-packing principle as the crystals of neutral molecules?

(ii) What is the relationship between ion size, shape, and stoichiometric ratio and the packing motif in crystalline cluster salts?

(iii) Are there preferential packing motives adopted in crystalline salts with respect to crystals of neutral molecules? (I.e. is there a detectable packing effect of the presence of the anion and cation charges?)

Our approach to these problems is basically the same as that applied previously to neutral species. It makes use of potential energy calculations within the pairwise atom–atom method (though only as a convenient tool to investigate packing relationships) and relies heavily on (commonly available) molecular graphics software.

Structure of High-Nuclearity Carbonyl Cluster Crystalline Salts and Methodology

As a first step toward the understanding of the factors controlling the ion interplay in these "soft salts", we have chosen to study two families of well-characterized high-nuclearity carbonyl clusters, namely that of the decametallic species containing a 1:3:6 close-packed arrangement of metal atoms (a tetracapped octahedron),[13-18] whose prototypical species is represented by the dianion $[Os_{10}C(CO)_{24}]^{2-}$,[13] and that of the hexametallic trigonal-prismatic clusters,[19-23] the prototype being represented by the dianion $[Rh_6C(CO)_{15}]^{2-}$.[23] The criterion for this choice has been 2-fold: on one hand, we needed carbonyl clusters with a highly regular ligand distribution; on the other hand, we needed species for which it is possible to vary the anionic charge without affecting the overall electron counting (i.e. isoelectronic species) and with minimum perturbation of the gross cluster anion shape (i.e. nearly isostructural species). In this respect, these two families of compounds are excellent candidates because the actual free charge can be changed by varying the nature of the interstitial atoms (carbon or nitrogen in the M_6 species) or the number of peripheral (or interstitial) H-hydride atoms (from 1 to 4 in the M_{10} family) with limited effects on the CO-ligand distribution.

What is more, these two groups of complexes have been characterized in a variety of crystalline salts with different counterions. The species subjected to our analysis are listed in Table I, together with relevant structural and crystallographic information and the references to the original structural reports. The recently characterized neutral cluster $[H_2Os_{10}C(CO)_{24}]$[17] is also reported for comparative purpose (see below).

Our approach to crystal packing is not conventional. In order to decode the ion organization within the lattice, we need to neglect, in a sense, the space group symmetry and concentrate on what the single ion (or molecule) "sees" around itself in its immediate neighborhood. This is not easily achieved with the usual crystallographic procedures (essentially based on intermolecular contact distances) and becomes particularly difficult with crystalline salts where the asymmetric unit contains two or three independent ions of large size. To carry out this study, we have, therefore, "adapted" the pairwise atom–atom packing potential energy method,[24] successfully employed previously to investigate the molecular organization in the lattice of neutral organometallic species.[8-11] Use is made of the expression ppe = $\sum_i\sum_j[A\exp(-Br_{ij}) - Cr_{ij}^{-6}]$, where ppe represents the packing potential energy[24] and r_{ij} the nonbonded atom–atom intermolecular distance. Index *i* in the summation runs over all atoms of one cluster anion (chosen as reference), and index *j*, over the atoms of the surrounding anions and/or cations distributed according to crystal symmetry in the crystal lattice within the cutoff distance of 15 Å. By this method the anions or cations in the first coordination sphere around the cluster anion chosen as reference can be easily selected among all the surrounding ions on the basis of the highest contribution to ppe. Since this procedure is used only as a convenient tool for the investigation of the cluster anion environment *and not* as a means to obtain (even approximate) crystal potential energy values, no attempt has been made to incorporate in the calculations the Coulombic contribution arising from the actual ionic charges. All calculations were carried out

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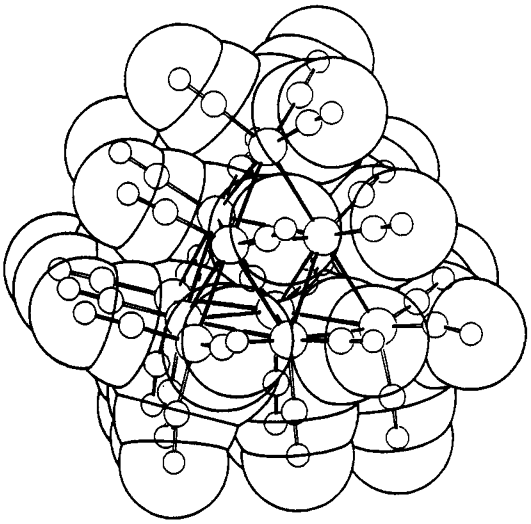

Figure 1. Structure of the dianion $[M_{10}C(CO)_{24}]^{2-}$ (M = Os, Ru),[13,15] showing the tetracapped octahedral metal atom cluster and the CO-ligand distribution. The outer shape of the cluster is represented by the space-filling outline.

with the aid of a slightly modified version of the computer program OPEC.[25a] SCHAKAL88[25b] was used for the graphical representation of the results.

Decametallic Family

The structure of the prototype in this family, the dianion $[Os_{10}C(CO)_{24}]^{2-}$,[13] is shown in Figure 1. While its metal framework and ligand distribution are well-known and will not be further discussed here, a brief description of the "outer shape" of the anion is necessary for the following discussion. The cluster shape is defined by essentially three "shape elements": (i) the tricarbonyl units on the apices; (ii) the six "grooves", each formed by two sets of three parallel CO's along the cluster edges, and (iii) the layers of close-packed six parallel CO's covering the triangulated faces (see Figure 1).

All decametallic species listed in Table I share these shape features (we have not considered the various derivatives whose decametallic frame does not correspond to a tetracapped octahedron or whose CO's are replaced by nonisosteric ligands). Our "sample" contains neutral, monoanionic, and dianionic species differing essentially for the number of H(hydride) atoms and the presence (or absence) of an interstitial carbide ligand. We have also not included in our analysis the species $[HRu_{10}C(CO)_{24}][PPN]$ and $[Ru_{10}C(CO)_{24}][PPN]_2{\cdot}C_6H_{14}$,[26] whose coordinates are not available either in the original papers or in the Cambridge Data Base.

A preliminary observation with respect to Table I is that all $[PPN]^+$ salts of the dianionic complexes are isomorphous. These triclinic crystals share the same basic packing motif: the dianions pile up along the *c* axis forming rows of tightly interlocked dianions which extend throughout the lattice (see Figure 2a). The dianion interlocking is based on what we have designated the "orthogonal" mode[17] (see Figure 2b). This very interaction was first observed in crystals of the neutral dihydride $[H_2Os_{10}C(CO)_{24}]$ (see Figure 2d), where it acts as the backbone of the whole lattice and involves the Os–Os bonds carrying the bridging-hydride ligands.[17] Therefore, the $\langle M_{10}(CO)_{24}\rangle$ fragment establishes *exactly* the same type of interlocking pattern in the crystals of the neutral molecule and of the dianions.

As shown in Figure 2a,c, the $[PPN]^+$ cations are also intimately interlocked and form a belt around the dianion pile. Apart for the rather obvious difference arising from the fact that the neutral molecule is surrounded by identical units in its lattice while the crystalline salt has to cope with the presence of the $[PPN]^+$ cations, the main difference between the crystals of the neutral complex and of the dianions is in the intermolecular separation along the piles (each molecule or anion is related to the next one by pure translational symmetry). The distance between the centers of mass (roughly the centers of octahedral cavities) is shorter in crystalline $[H_2Os_{10}C(CO)_{24}]$ (9.980 Å) than in the dianion salts (from 10.444 to 10.601 Å; see Table I). However, it is difficult to say whether the lengthening of the interanion separation with respect to that between the neutral molecules is a consequence of interanion electrostatic repulsions or is caused by the need of efficient interlocking with the surrounding cations. It is also noteworthy that the intermolecular O···O contact distances are strictly comparable in the two crystals [shortest next-neighbor O···O separations in the range 2.96–3.06 Å between Os_{10} dianions versus 2.98–3.10 Å between neutral molecules] confirming that the dianions establish "normal" van der Waals contacts in spite of the ionic charge (see also below).

Altogether these crystal salts can be described in a pictorial way as constituted of "coaxial cluster cables" extending along the *c* axis.

The crystal structure of $[Os_{10}C(CO)_{22}(NO)(I)]^{2-}$ also deserves comment in the light of these observations. The terminally bound I ligand was reported to be disordered over two sites with equal occupancy.[16] These sites belong to the edges involved in the "orthogonal" interactions linking the anions along the piles. The *pseudo*-2-fold axis of the disorder model[16] is coincident with the pile axis. We now know that the anion–anion linkage along the pile does not differ if the I ligand occupies one site or its symmetry-related one over the grooved cluster edge, thus resulting in the observed space-averaged disordered structural model.

The ion organization is quite different in the crystals of the monoanion $[HOs_{10}C(CO)_{24}]^-$. In the $[Ph_3MeP]^+$ salt anion piles are still present although each pile is not "insulated" from the others by a cation belt but interacts directly with other three piles (see Figure 3a). The anions are "apex-to-base" linked via the interaction of one tricarbonyl unit of one anion with the triangular face of a neighboring anion along the *c* axis of the triclinic cell (see Figure 3c). The anions of the central pile are related to those of the surrounding ones by crystallographic inversion centers. The near 3-fold symmetry of this packing distribution is clearly reflected in the near hexagonal values of the cell parameters (see Table I). Interestingly, this trigonal pattern becomes actual crystallographic symmetry in the $[Ph_4As]^+$ salt of the same monoanion (see Figure 3b). As a matter of fact, the anion distribution in this latter salt is closely related to that observed in the $[Ph_3MeP]^+$ salt: piles of "apex-to-base" linked monoanions extend along the *c* axis, as shown in Figure 3d. The anions along the piles have the same orientation with respect to the cell axis. The "apex-to-base" interaction is slightly

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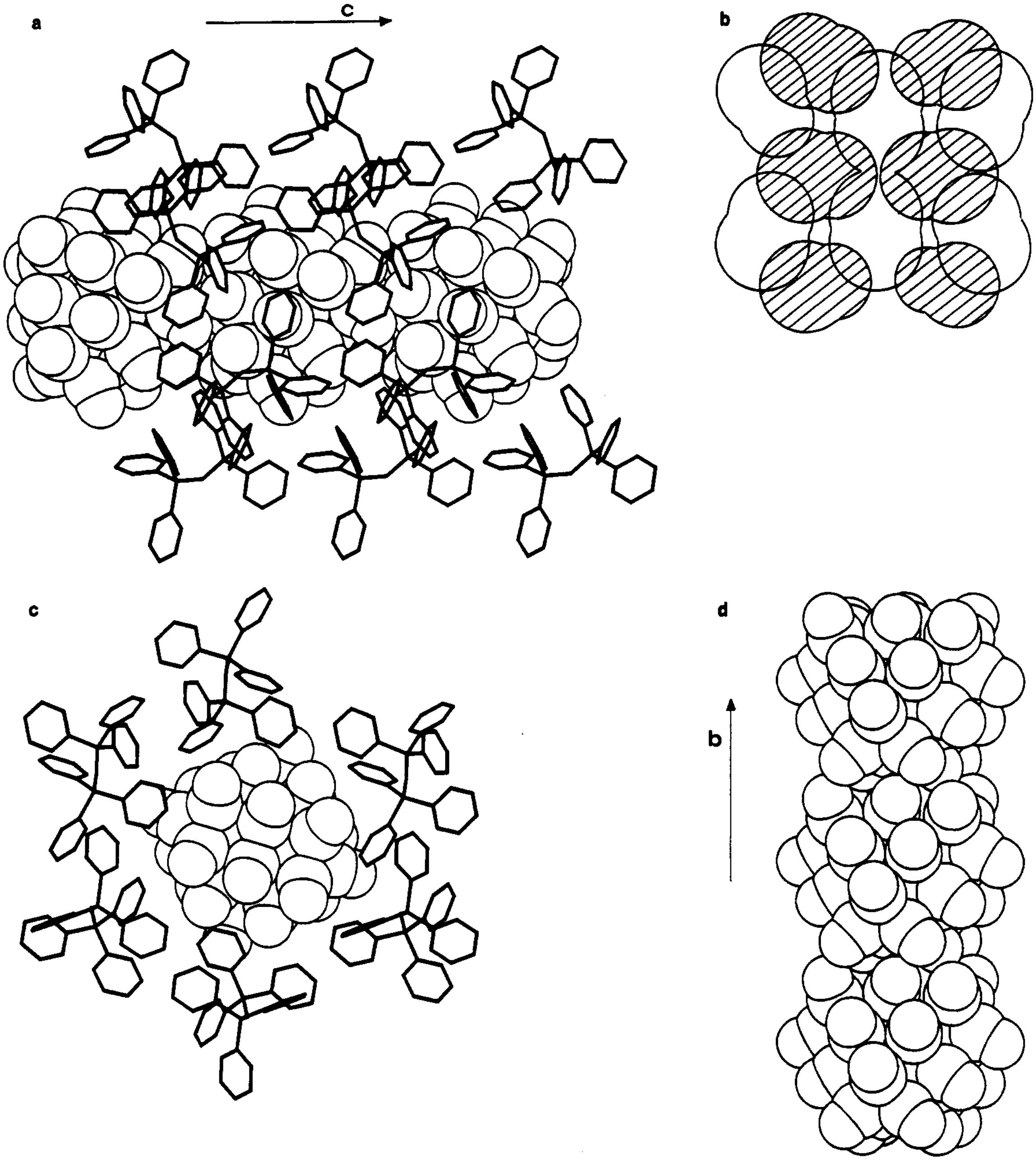

Figure 2. Ion organization in the decametallic dianions: (a) pile of M_{10} dianions extending along the *c* axis of the triclinic cell and surrounded by the $[PPN]^+$ cations; (b) sections showing the "orthogonal" interlocking mode linking consecutive dianions (empty and shaded outlines) along the pile; (c) view down the pile axis showing the cation belt (the "coaxial cluster cable"); (d) molecular pile present along the *b* axis in crystalline $[H_2Os_{10}C(CO)_{24}]$[17] (compare with (a)).

different in the two crystals: the exact anion superimposition required by the crystallographic symmetry in the $[Ph_4As]^+$ salt puts the O atoms of two consecutive anions face to face, while a small tilting of the anions allows some degree of CO···CO compenetration in the $[Ph_3MeP]^+$ salt. As a consequence, the interanion separation is shorter in this latter salt (12.016 Å) than in the former (12.070 Å). As observed for the dianion $[Os_{10}C(CO)_{24}]^{2-}$, O···O contacts along the pile are quite short (shortest next neighbors 2.86 and 3.08 Å in the $[Ph_4As]^+$ and $[Ph_3MeP]^+$ salts, respectively) and comparable with those observed in crystals of neutral molecules.

The different interlocking attained via the "apex-to-base" with respect to the "edge-to-edge" (orthogonal) interlocking discussed above is reflected in the interanion separation: the distance between the centers of two consecutive anions in the salts of the two monoanions is much longer than in the crystals of the neutral species and of the dianions (12.016–12.070 Å versus 9.890–10.601 Å; see Table I).

In both monoanion salts the counterions fill in the channels left in between the anion piles, thus forming cations rows. It is difficult to understand, however, why an ordered distribution of the cations is possible with the $[Ph_3MeP]^+$ cation while disorder in the cation distribution is present in the $[Ph_4As]^+$ salt.[18b]

Hexametallic Prismatic Family

The structure of the prototypical anion in this family, namely $[Rh_6C(CO)_{15}]^{2-}$, is shown in Figure 4. Although no comparison with an isoelectronic neutral derivative is possible, three different salts of the isostructural and isoelectronic dianions $[M_6C(CO)_{15}]^{2-}$ (M = Co, Rh) are available: the $[(PhCH_2)Me_3N]^+$ salt for both Co and Rh complexes, the $[PPh_4]^+$ salt for M = Rh, and the $[Et_4N]^+$

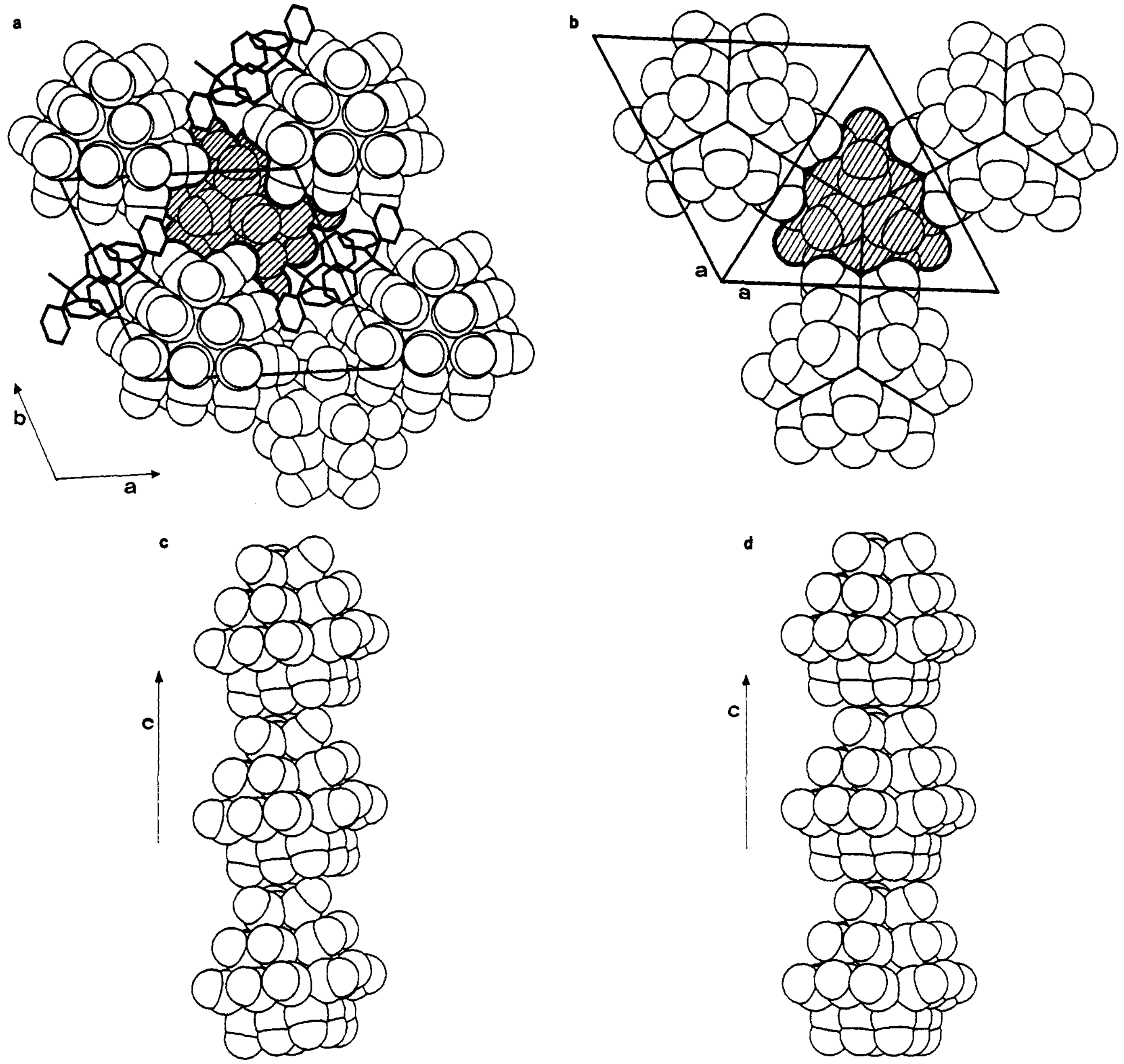

Figure 3. Ion organization in crystalline $[HOs_{10}C(CO)_{24}][Ph_3MeP]$ and $[HOs_{10}C(CO)_{24}][Ph_4As]$: (a) projection down the *c* axis in the triclinic cell of the salt $[HOs_{10}C(CO)_{24}][Ph_3MeP]$, showing the nearly trigonal symmetry and the distribution of the anions piles; (b) projection down the *c* axis in the hexagonal cell of the salt $[HOs_{10}C(CO)_{24}][Ph_4As]$, where the $[Ph_4As]^+$ cations (not shown because of the disorder[18b]) occupy the "interstices" between the anions; (c) a pile of $[HOs_{10}C(CO)_{24}]^-$ anions in the lattice of the $[Ph_3MeP]^+$ salt, showing how the anions are linked via "apex-to-base" interactions; (d) a pile of $[HOs_{10}C(CO)_{24}]^-$ anions in the lattice of the $[Ph_4As]^+$ salt.

salt for M = Co. Furthermore the $[PPN]^+$ salts of the isoelectronic monoanions $[M_6N(CO)_{15}]^-$ (M = Co, Rh) are known. The information on this family of anions is collected in Table I.

A further point of structural interest has a direct chemical origin: it is known that the dianions undergo selective electrophilic addition at the triangular faces of the metal prism. This behavior, together with the evident "displacement" of the CO ligands away from the middle of the faces (see Figure 4), has been attributed to the localization of charge density over these sites.[19] We wish to ascertain whether this charge localization has any detectable effect on the molecular organization within the lattice.

In the *monoclinic* $[Et_4N]^+$ *salt the dianions* $[Co_6C(CO)_{15}]^{2-}$ are arranged in a way which closely recalls that observed for the Os_{10} (and Ru_{10}) dianions. As shown in Figure 5a, the lattice contains anionic piles surrounded by a cation belt. However, the dianions are not exactly superimposed but shifted in a staircaselike pattern (see Figure 5b). The shift allows compenetration and interlocking of the terminal CO ligands belonging to two contiguous prisms, without involving the centers of the triangular faces. O···O next-neighbor contacts are rather long ranging from 3.24 to 3.26 Å. The cations, on the other hand, appear to direct one of the CH_3 termini toward the middle of the triangular faces.

The tendence to form anionic piles is also confirmed by the $[M_6N(CO)_{15}][PPN]$ salts (M = Co, Rh). The packing observed for the $[Et_4N]^+$ salt of the $[Co_6C(CO)_{15}]^{2-}$ dianion is essentially retained in these crystals, although the different *stoichiometric ratio necessitates* a denser packing of the monoanions resulting in close contacts between the anionic piles (see Figure 6a). The relationship between

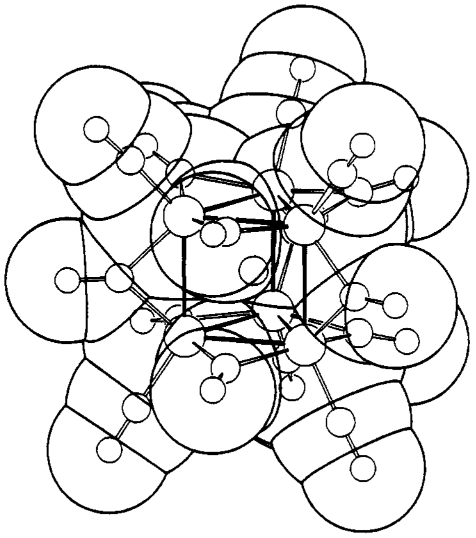

Figure 4. Structure of the dianion $[M_6C(CO)_{15}]^{2-}$ (M = Co, Rh),[22,23] showing the CO-ligand distribution and the trigonal-prismatic metal atom framework. The space-filling outline shows how the ligands are tightly packed over the square faces, while a large niche is left in the middle of the prism triangular faces.

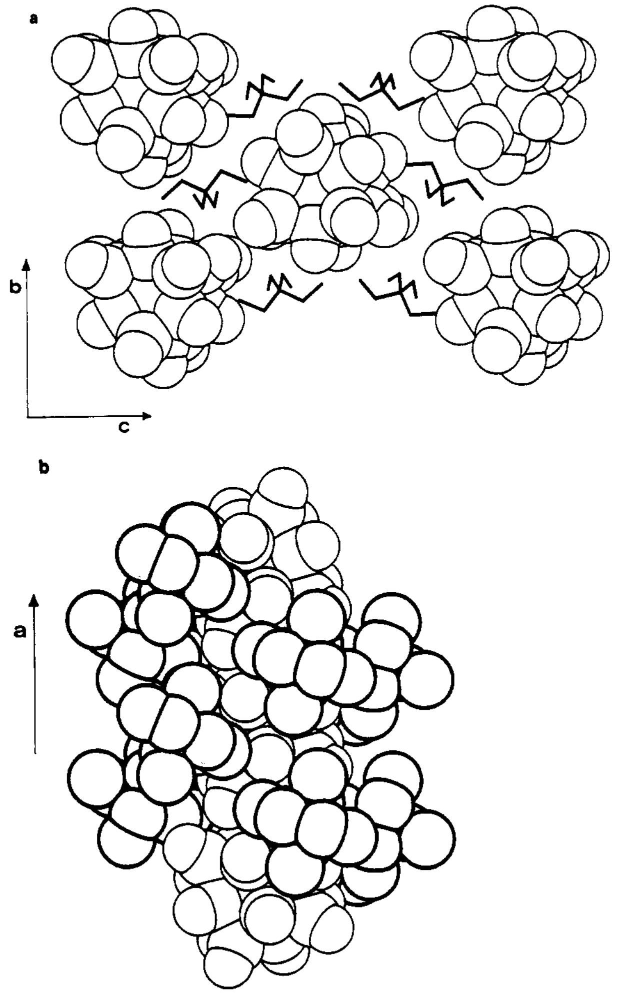

Figure 5. Ion organization in crystalline $[Co_6C(CO)_{15}][Et_4N]_2$: (a) projection down the a axis, showing how the anion piles are surrounded by a belt of $[Et_4N]^+$ cations; (b) side view of the anion pile, showing the staircaselike pattern and the folding of the cation belt.

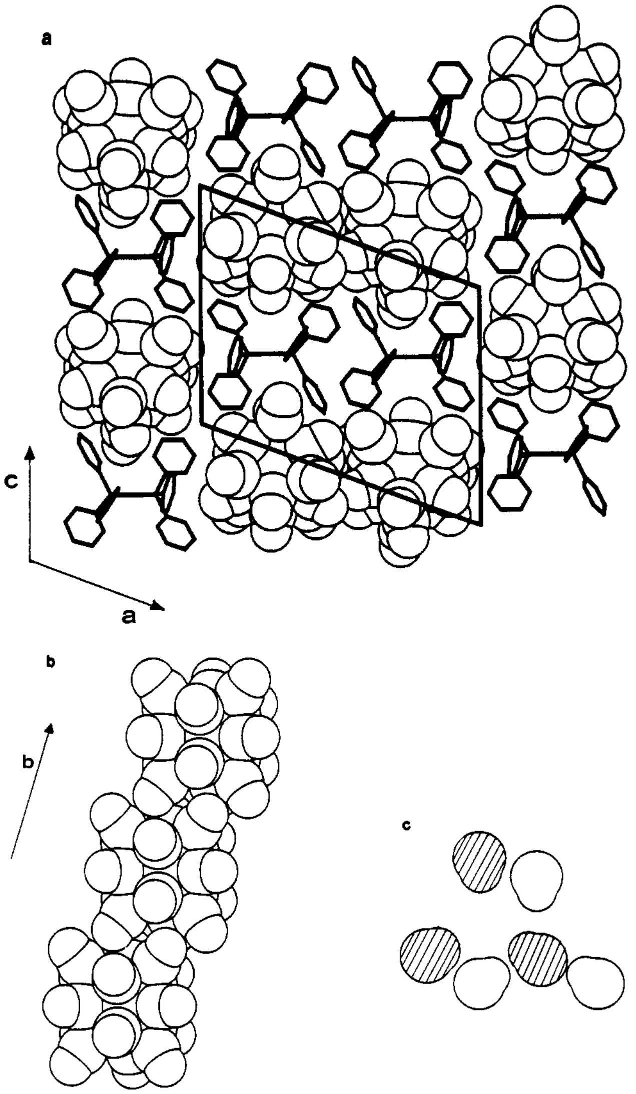

Figure 6. Ion organization in crystalline $[M_6N(CO)_{15}][PPN]$: (a) projection down the b axis in the triclinic cell, showing the close contact between the monoanion piles; (b) side view of the anion pile, showing the staircaselike pattern (compare with Figure 5b); (c) sections cut between two consecutive dianions (emtpy and shaded outlines), showing the CO···CO interlocking.

the ion packing in these hexanuclear cluster salts is, therefore, very much the same as that discussed above for the decametallic clusters; i.e., on increase of the anion/cation ratio, the tendency to form anionic piles is mantained, but the piles are brought in close proximity. Figure 6b shows the staircaselike pattern (compare with Figure 5b), while Figure 6c shows the effective compenetration of the terminal CO ligands, yielding O···O contact distances as short as 3.03 Å (M = Rh), the CO ligands being actually closer to the triangular face midpoint than in the dianion case.

The situation is different in the triclinic cell of $[Rh_6C(CO)_{15}][Ph_4P]_2$. Although one can still observe piles of anions along the c axis completely embedded in a belt of $[Ph_4P]^+$ cations (see Figure 7a), the dianion–dianion interaction along the pile involves CO ligands covering the square faces of the prisms, so that the triangular faces are directed toward the surrounding cations. The anions are not quite in contact (see Figure 7b), the interanion separation being 11.339 Å (i.e. longer than in any other crystal of hexanuclear species). The cation–cation interaction is based on an intimate intermixing of the phenyl groups.

Finally, we wish to comment on the ion organization in the isomorphous crystals of $[M_6C(CO)_{15}][(PhCH_2)Me_3N]_2$ (M = Co, Rh). These crystals are, in a sense, exceptional in that "true" anion–cation interactions are established.

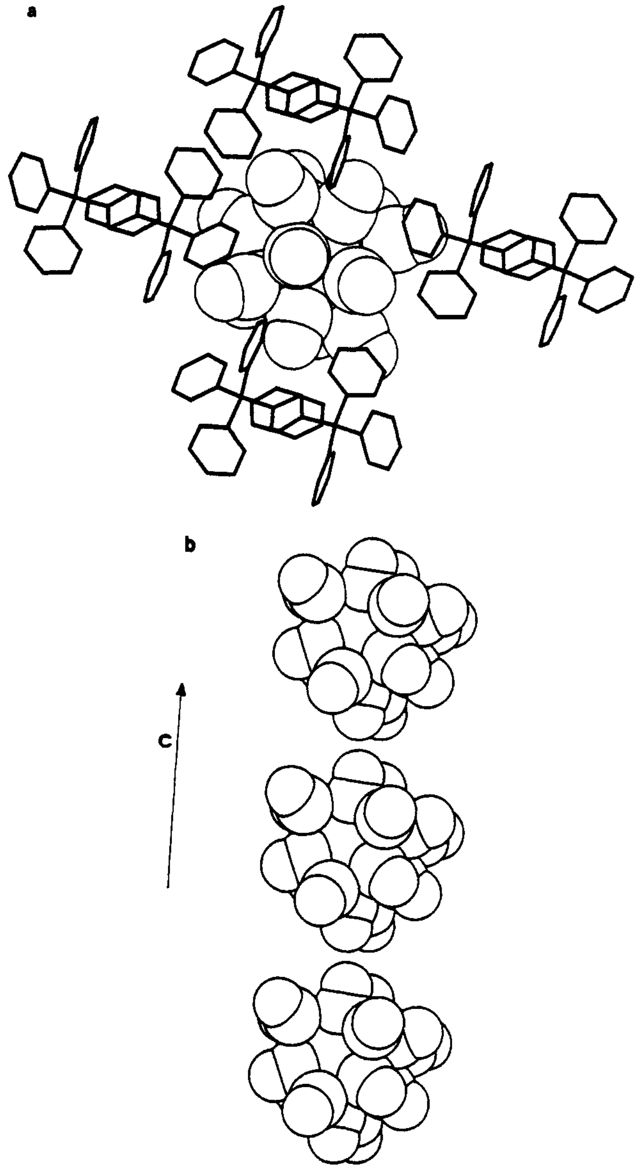

Figure 7. Ion organization in crystalline $[Rh_6C(CO)_{15}][Ph_4P]_2$: (a) pile of dianions surrounded by $[Ph_4P]^+$ cations viewed down the *c* axis in the triclinic cell; (b) dianion stacking along the unit cell *c* axis.

As shown in Figure 8a, the $[M_6C(CO)_{15}]^{2-}$ dianions are in direct contact via their triangular faces with the $[(PhCH_2)Me_3N]^+$ cations above and below, one methyl group actually penetrating the hollow site over these faces. Each trimeric $[M_6C(CO)_{15}][(PhCH_2)Me_3N]_2$ unit is arranged in the lattice (see Figure 8b) so that each anion is effectively surrounded by six counterions. Direct anion–cation interactions forbid tight anion–anion interlocking, resulting in only a few O···O contacts between neighboring anions (in the range 3.10–3.28 Å).

Concluding Remarks

With this paper we have begun to understand the factors controlling the structure of organometallic salts containing large cluster anions. Quite unexpectedly, we have observed that, irrespective of the metal core nuclearity and of the actual ionic charge, cluster anions tend to form *monodimensional crystals within the tridimensional network*. This is achieved via tight interlocking of the CO ligands as observed in crystals of neutral carbonyl species.[8a] Intermolecular CO···CO contacts do not appear to be affected to any significant extent by the presence of the ionic charge.

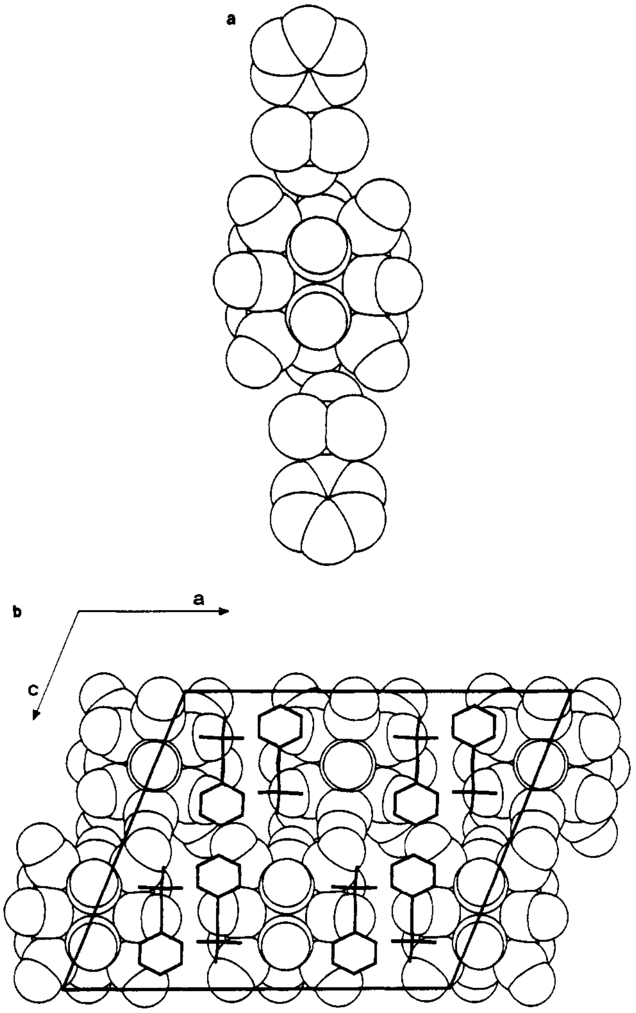

Figure 8. Ion organization in crystalline $[M_6C(CO)_{15}][(PhCH_2)Me_3N]_2$ (M = Co, Rh):[22,23] (a) direct cation–anion interaction via the prism triangular faces; (b) projection of the ion organization in the *ac* plane.

In the decametallic family we have found that anion–anion interlocking is based either on interactions along the idealized 2-fold symmetry axis of the $\langle M_{10}(CO)_{24}\rangle$ framework (dianions and neutral species) or along the 3-fold symmetry axis (monoanions), while anion–anion interlocking in the trigonal-prismatic species seems (at least in the case of the carbido dianions) to avoid the centers of the triangular faces which are supposed to carry negative charge density. It is difficult to say, however, if the staircaselike pattern results from the need to avoid superimposition of the triangular faces or from the need to allow closer interaction of these sites with the counterions. In general, when the anion–cation ratio is 1:2, and use is made of the large $[PPN]^+$, the anion piles are completely surrounded by counterions, while direct interpile contact is observed on decreasing the stoichiometric ratio to 1:1.

In summary, the ion organization in these crystalline salts appears to be governed essentially by the need to occupy space efficiently (i.e. to attain maximum van der Waals cohesion, as in typical molecular crystals formed by neutral molecules) with the (obvious) additional constraint imposed by the need to preserve electroneutrality of the material.

It would appear that these two conditions are best satisfied by forming monodimensional (or nearly so) anionic crystals by piling the cluster anions and by surrounding the anion rows with cations. To put it in a rather crude way, we can look at these crystals as cocrystals whose structure is governed mainly by the steric similarity between the anions on one side and between the cations on the other (i.e. the similar packs better with the similar). In the case of carbonyl anions this preference can be assigned to the more effective interlocking possible between molecules with surface CO ligands. This situation recalls that observed in crystalline carbonyl–arene neutral clusters,[11b] where the crystal building process has to cope with the simultaneous presence of CO ligands and of flat arene fragments. In such cases the most efficient arrangement is invariably attained by grouping together in the lattice the fragments having similar shape, i.e. arenes with arenes and CO's with CO's.

Our analysis is necessarily very much qualitative. However, we would like to stress that a careful investigation of the molecular or ion organization in the crystal is the basis on which solid-state studies must be founded. For instance, it is worth recalling that several conducting materials have strongly anisotropic physical properties. This anisotropy usually arises from the molecular arrangement in the lattice. In organic conductors and superconductors, low-dimensionality (i.e. stacks of planar molecules or molecular piles and strings) is a prerequisite for molecules or ions to carry electrons through the network.[28] Furthermore, several high-nuclearity clusters have been shown to possess physical properties distinct from both molecules and bulk metals (the "metametallic" state).[6,7]

We believe that, to be successful, the appreciation of the physical–chemical properties of these organometallic materials must rely not only on the knowledge of the structure of the component molecules or ions but also on information on the structure of the *entire* crystalline edifice.

Acknowledgment. Financial support by the Ministero della Università e della Ricerca Scientifica e Tecnologica is acknowledged.

Registry No. $[Os_{10}C(CO)_{24}][PPN]_2$, 75117-74-7; $[H_4Os_{10}(CO)_{24}][PPN]_2$, 110371-99-8; $[Ru_{10}C(CO)_{24}][PPN]_2$, 118977-37-0; $[Os_{10}C(CO)_{22}(NO)I][PPN]_2$, 100430-54-4; $[H_2Os_{10}C(CO)_{24}]$, 77908-36-2; $[HOs_{10}C(CO)_{24}][Ph_3MeP]$, 82609-29-8; $[HOs_{10}C(CO)_{24}][Ph_4As]$, 82609-28-7; $[Co_6C(CO)_{15}][Et_4N]_2$, 120224-09-1; $[Rh_6C(CO)_{15}][Ph_4P]_2$, 114714-06-6; $[Co_6N(CO)_{15}][PPN]$, 72782-99-1; $[Rh_6N(CO)_{15}][PPN]$, 85490-74-0; $[Co_6C(CO)_{15}][PhCH_2Me_3N]_2$, 53509-52-7; $[Rh_6C(CO)_{15}][PhCH_2Me_3N]_2$, 39357-18-1.

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Synthesis and Reactivity of $[(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2]Fe(CO)_3$

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Received August 21, 1991

Reaction of $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ (1) with (benzylideneacetone)$Fe(CO)_3$ gives $[(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2]Fe(CO)_3$ ((dfepe)$Fe(CO)_3$ (2)) in 59% yield. Photosubstitution of CO by L yields (dfepe)$Fe(CO)_2L$ (L = THF, $P(OCH_3)_3$, C_2H_4). The ethylene complex has been characterized by single-crystal X-ray analysis ($C_{14}H_8F_{20}FeO_2P_2$, monoclinic, $P2_1/c$, $a = 10.806$ (5) Å, $b = 14.069$ (5) Å, $c = 15.415$ (3) Å, $\beta = 101.61$ (2)°, $V = 2295.4$ (14) Å^3, and $Z = 4$) and shows an unusually short carbon–carbon double bond (1.362 (7) Å) indicating weak π-back-bonding. Photolysis of 2 under 1 atm of acetylene yields the cyclopentadienone complex (η^4-C_5H_4O)Fe(CO)(dfepe) while irradiation in the presence of butadiene yields (η^4-C_4H_6)Fe(CO)(dfepe). Three styrene complexes (η^6-C_8H_8)Fe(CO)(dfepe), (η^2-C_8H_8)$Fe(CO)_2$(dfepe), and (η^4-C_8H_8)Fe(CO)(dfepe) were isolated when 2 was photolyzed in the presence of styrene. The structure of the η^4-styrene complex was verified by a single-crystal X-ray analysis ($C_{19}H_{12}F_{20}FeOP_2$, triclinic, $P\bar{1}$, $a = 8.7382$ (16) Å, $b = 10.789$ (3) Å, $c = 15.652$ (6) Å, $\alpha = 87.382$ (16)°, $\beta = 101.61$ (2)°, $\gamma = 73.857$ (17)°, $V = 1262.9$ (6) Å^3, and $Z = 2$). The η^4-styrene complex can be used as an efficient (dfepe)Fe(CO)-transfer agent. Photolysis of 2 under 1 atm of H_2 gave the fluxional *cis*-dihydride complex (dfepe)$(CO)_2Fe(H)_2$ (17). Attempted oxidative addition of Et_3SiH to photogenerated (dfepe)$Fe(CO)_2$ gave dihydride complex 17 and $(Et_3Si)_2O$. Photolysis of 2 in alkane solvents at temperatures from −50 to +25 °C gave no evidence for oxidative addition adducts.

Introduction

There are a limited number of bidentate ligands with strong π-accepting properties available for use in synthesis and stabilization of low-valent transition-metal complexes.[1-7] An attractive class of such ligands is the perfluorinated bidentate alkyl phosphines, $(R_f)_2PCF_2CF_2P(R_f)_2$ (R_f = perfluoroalkyl). It is well-established that $(CF_3)_3P$ is similar to CO in its π-acceptor properties, and thus $(R_f)_2PCF_2CF_2P(R_f)_2$ complexes represent chelates which should mimic the electronic properties of two cis carbonyl ligands. Aside from the usual advantages of chelates, several other features of these ligands are of interest: (1) The steric bulk of the ligands can be varied by changing R_f. (2) The presence of highly lipophilic R_f

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