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Molecular Orbital Calculations on Model Fe(CO)$_2$L(η^4-enone) Complexes with L = CO, PH$_3$, and P(OH)$_3$. Electronic and Steric Effects in Fe(CO)$_2$L(η^4-benzylideneacetone)

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The bonding properties of the model complexes Fe(CO)$_2$L(η^4-butadiene) and Fe(CO)$_2$L(η^4-enone) with L = CO, PH$_3$, and P(OH)$_3$ were studied. The characteristics of the frontier orbitals of the Fe(CO)$_2$L fragments determine their interaction with the butadiene and enone ligands completing the metal coordination sphere. The frontier orbitals of butadiene are stabilized when one CH$_2$ is replaced by the more electronegative oxygen atom. The staggered conformation is preferred by the Fe(CO)$_3$(η^4-enone) complexes. The most stable of the three possible staggered conformations of Fe(CO)$_2$L(η^4-enone) is the one in which the phosphorus ligand is approximately trans to the central C–C bond of the enone. The strongest interaction between the enone and Fe(CO)$_2$L is back-donation from the HOMO of the metal fragment to the empty π_3 orbital of the enone, more electrons thus being donated than received by the metal. Electron density is mainly lost by the oxygen atom and gained by the terminal carbon atom (C$_4$) of the enone. The results were used to interpret the isomer distribution in Fe(CO)$_2$L(η^4-enone) and the electronic effects in Fe(CO)$_2$L(η^4-benzylideneacetone) complexes where L is CO, phosphine, and phosphite.

Introduction

Iron carbonyl complexes of olefinic ligands are of considerable interest in organic synthesis.[1] The Fe(CO)$_3$ moiety activates coordinated dienes toward nucleophilic attack, stabilizes allyl and dienyl carbonium ions, and may act as a protecting, activating, or directing group in several reactions. Cyclic and acyclic Fe(CO)$_3$(diene) and [Fe(CO)$_3$(dienyl)]X complexes show high stereo- and regiospecificity in reactions with both nucleophiles and electrophiles.[2-4]

Several theoretical studies[5-9] helped the understanding of the nature of the iron–diene bonding and the mechanism of action of the Fe(CO)$_3$ fragment. In particular the complex Fe(CO)$_3$(butadiene) has been theoretically studied by several methods and the results of those studies have been compared to experimental data (rotation barriers, photoelectron spectra, etc.).[5-7]

Many complexes containing an iron atom coordinated to two carbonyl groups, one phosphorus ligand, and a diene have been prepared,[10-17] and some of these complexes show both increased reactivity toward electrophiles[18] and pronounced differences in regiospecificity of nucleophilic attack[16] relative to the case for the analogous Fe(CO)$_3$ derivatives. Iron dicarbonyl phosphine and iron dicarbonyl phosphite complexes containing an enone ligand have been also prepared and studied.[14,19-21] Solid-state X-ray studies of Fe(CO)$_2$(PPh$_3$)(η^4-cyclodiene)[15] and Fe(CO)$_2$L(η^4-benzylideneacetone) (L = PPh$_3$, PEt$_3$)[19] show that the iron atom adopts a distorted-octahedral coordination geometry in which three facial sites are occupied by the diene or enone. The two carbonyl groups are cis to each other, while the phosphine is approximately trans to the midpoint of the internal C–C bond of the diene or enone. Phosphorus-31 magnetic resonance studies of Fe(CO)$_2$L(η^4-enone) (L = phosphine, phosphite)[21] have shown that these complexes exist in solution as interconvertible isomeric mixtures with L in the position trans to the midpoint of the internal C–C bond (axial isomer) or in one of the equatorial positions with respect to the C–C bond. A bonding model was proposed on the basis of a carbon-13 magnetic resonance study[20] of Fe(CO)$_2$L(bda) (bda = benzylideneacetone; L = phosphines, phosphites) in which the coordinated bda acts as a "sink" for the negative charge placed in the iron atom by the phosphinated ligand via a P→Fe→bda mechanism.

In this paper we present a theoretical study of the bonding properties and fluxional behavior of the model complexes Fe(CO)$_2$L(η^4-butadiene) and Fe(CO)$_2$L(η^4-enone) with L = PH$_3$ and P(OH)$_3$, which will be based on extended Hückel molecular orbital calculations.[21] Details are given in the Appendix. A discussion of electronic and

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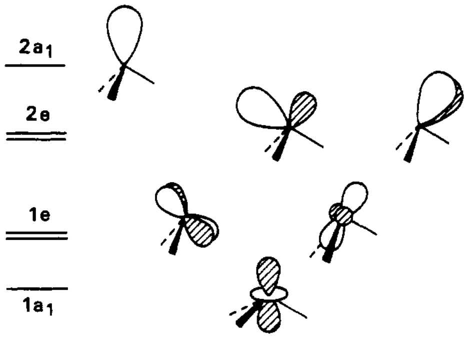
steric properties of Fe(CO)$_2$L(η^4-enone) (L = CO, phosphines, phosphites) is also presented.

Results and Discussion

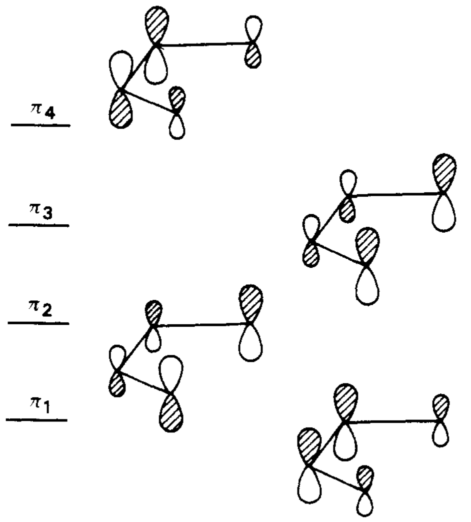
Fe(CO)$_2$L Fragment. The Fe(CO)$_3$ fragment has been well studied, and its bonding to butadiene is described in the literature.[5-7] Let us then consider this fragment. It can be derived from a hypothetical octahedral Fe(CO)$_3$L$_3$ complex by taking away the three L ligands (assuming they are on one face; the C–Fe–C angles are 90°). The 3-fold symmetry axis that remains is taken as the z axis. The frontier orbitals of this fragment (**1**) are related to those of an octahedral species.



1

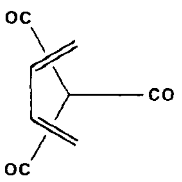
The splitting of the d orbitals is such that there is a set of three lower energy levels, derived from t$_{2g}$, and a set of two higher energy levels, derived from e$_g$. However, due to the coordinate system chosen, there is mixing between $x^2 - y^2/yz$ and xy/xz. Higher in energy lies an empty sp hybrid orbital.[7-9]

For a d^8 low-spin Fe(CO)$_3$ fragment, the three lower levels, 1a and 1e, are filled and there are two electrons in the 2e levels. The strongest interactions occur between the 2e orbitals and butadiene π_2 and π_3 orbitals (the four π butadiene orbitals are shown in **2**), the net result being an electron transfer from the iron carbonyl fragment to the diene.



2

The rotation barrier for this complex has been experimentally determined,[23] and the electronic reasons for the preferred staggered geometry **3** lie mainly in a better overlap between the tilted orbitals on Fe(CO)$_3$ and the butadiene orbitals.[24] This difference in overlap is represented in **4** for one important molecular orbital in the staggered and in the eclipsed geometries.



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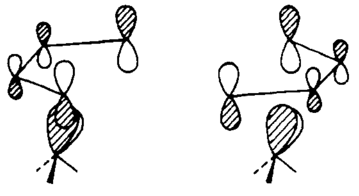

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Let us now consider what happens when a carbonyl group is replaced by a phosphine. The degeneracy of the e levels is destroyed, owing to the decrease in symmetry (the 3-fold symmetry axis disappears; only a mirror plane remains). The wave function contours of the frontier orbitals of the new Fe(CO)$_2$(PH$_3$) fragment are shown in Figure 1 and can be compared to those of Fe(CO)$_3$.[9]

Changes in energy (in the former 1e set, 2e$_a$ and 2a$_1$) arise from the difference between a carbonyl and a phosphine: introduction of PH$_3$ raises the energy of many orbitals, making the Fe(CO)$_2$(PH$_3$) fragment a better donor and a weaker acceptor. The relative energies of the frontier orbitals for the Fe(CO)$_2$L fragments are represented in Figure 2. The composition of the orbitals is also changed. The three lower energy levels, 1a$_1$ and 1e, are bonding orbitals involved in back-donation from iron to the three carbonyls. When a phosphine ligand is introduced, the acceptor orbitals have almost no contribution from it, meaning that they are localized only on two ligands, the carbonyls. Also, z^2 has now the same symmetry as $x^2 - y^2$, so they mix. As a result, there are significant changes in composition for these orbitals, especially 1a$_1$(z^2), which becomes $x^2 - y^2$ with some mixed z^2.

The three higher energy levels, 2e and 2a$_1$, are antibonding molecular orbitals arising from interactions between carbonyl and phosphine filled orbitals (2e) and metal orbitals or empty ligand orbitals and z^2, their antibonding character being relieved by admixture of empty high-energy iron p orbitals. They are very similar to those of Fe(CO)$_3$, as far as composition is concerned. The antisymmetric orbital of the 2e set, however, is destabilized by the introduction of the phosphine. There was some mixing of carbonyl π^*, which decreased its antibonding character. When a phosphine is coordinated, there are no orbitals of the right symmetry available. 2a″ has a higher energy than 2e(a″).

The third fragment we are going to consider is Fe(CO)$_2$(P(OH)$_3$), containing a phosphite ligand. The energies of its frontier orbitals are shown in Figure 2, along with those of Fe(CO)$_3$ and Fe(CO)$_2$(PH$_3$). Most of them lie between the orbitals of the other two fragments, which is due to the presence of the electronegative oxygen atoms attached to phosphorus.

The greatest change as one goes from Fe(CO)$_2$(PH$_3$) to Fe(CO)$_2$(P(OH)$_3$) occurs for 3a′, which is more destabilized,

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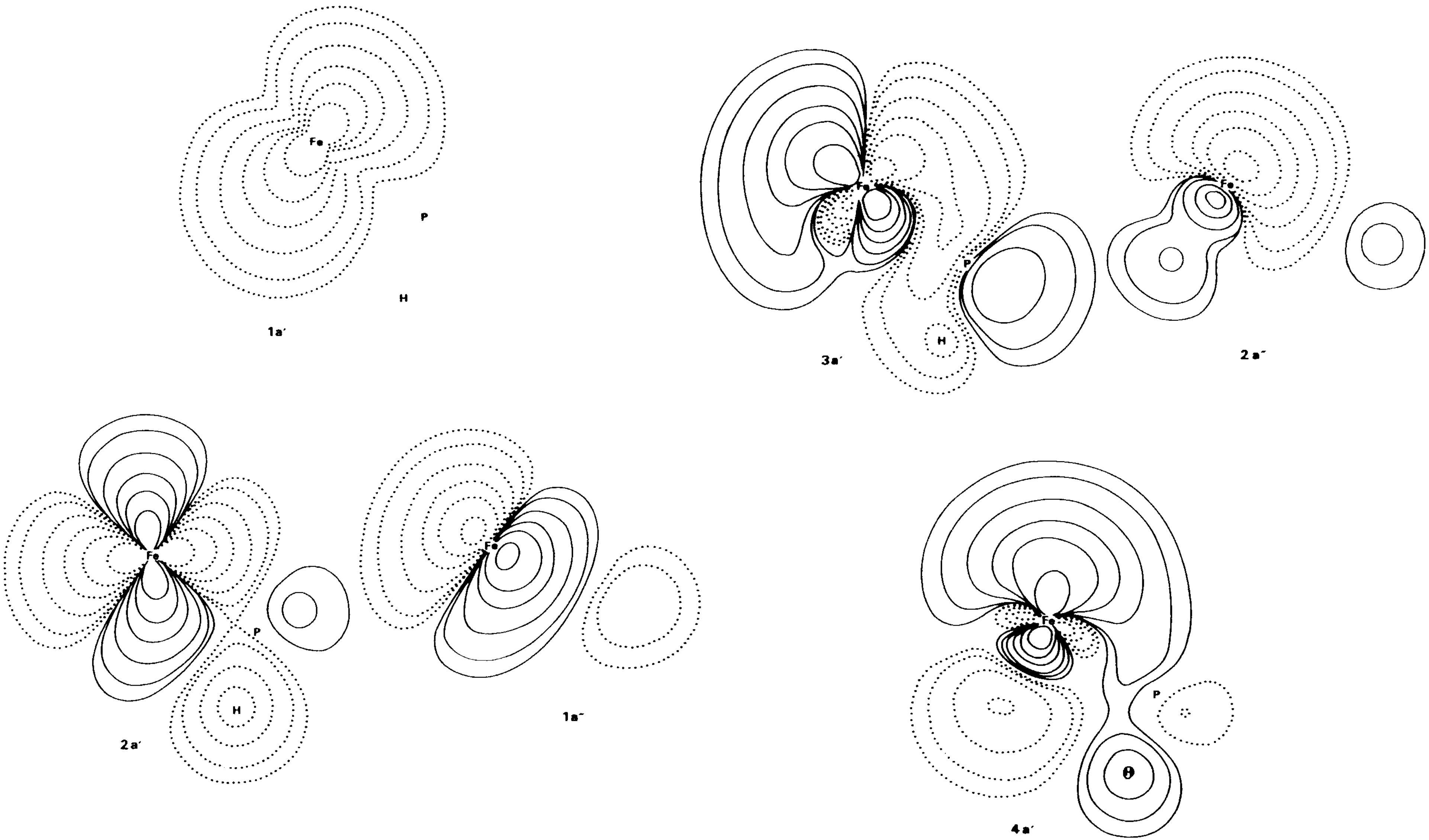


Figure 1. Plot of the frontier orbitals of a $Fe(CO)_2(PH_3)$ fragment in the xz plane (values for Ψ are 0.2, 0:1, 0.055, 0.025, 0.010, and 0.005; solid lines indicate positive Ψ and dashed lines negative Ψ). 1a″ and 2a″ are plotted in a plane parallel to xz, 0.5 Å away in the y direction, as they have a node in xz.

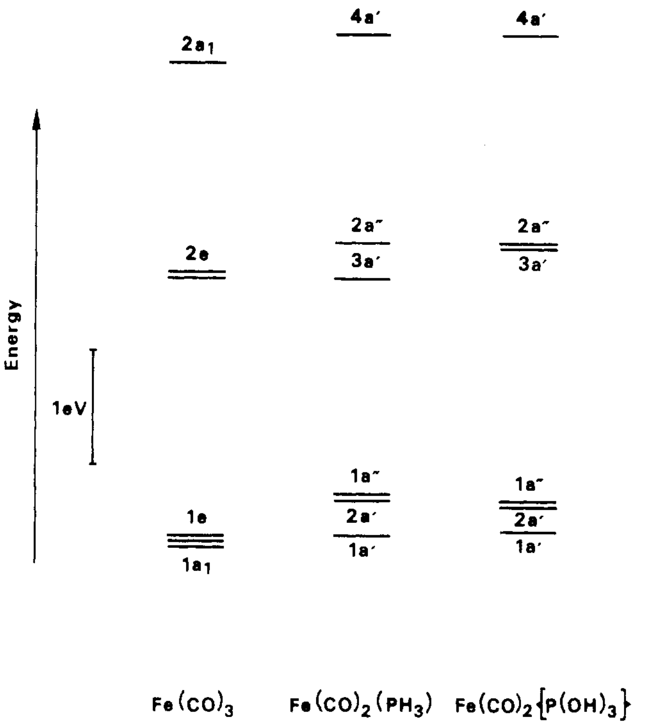
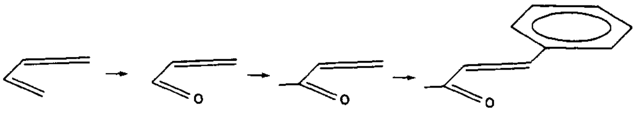


Figure 2. Energies of the frontier orbitals of the fragments Fe(CO)$_2$L (L = CO, PH$_3$, P(OH)$_3$).

implying a better donor capacity for the fragment. This reflects the higher energy of the phosphite lone pair relative to that of the phosphine. The other occupied orbitals and the empty orbitals are very similar to those of Fe(CO)$_2$(PH$_3$).

Enone Ligands. The orbitals of butadiene were shown earlier (2). They are going to be changed when a CH$_2$ group is replaced by an oxygen, in what can be considered as the first and most important step in going from butadiene, CH$_2$═CH—CH═CH$_2$, to benzylideneacetone (bda) (5).



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The introduction of methyl and phenyl substituents does not alter the orbitals so dramatically.

Replacing CH$_2$ by the more electronegative oxygen atom leads to a general stabilization of the orbitals, with an increased oxygen participation in the lower energy orbitals, while the higher energy ones become more strongly localized in the carbon atoms. Besides, oxygen has a lone pair, at an energy close to that of π_1. The orbitals of the species represented in 5 and their relative energies are given in Figure 3. The orbital to which we can assign the oxygen lone-pair character is shown for CH$_2$═CH—CH═O.

The best acceptor orbital, π_3, becomes more localized in carbon atoms C$_2$ and C$_4$ (6), while the main contribution to the donor orbital π_2 comes from C$_3$. Oxygen has the strongest participation in π_1. Introduction of methyl and phenyl substituents causes only minor changes in the orbitals, both in energy and in composition, as can be seen in Figure 3. Their influence on the complex will be mainly steric. The diene containing an oxygen atom is going to behave as both a better acceptor and a weaker donor than butadiene.

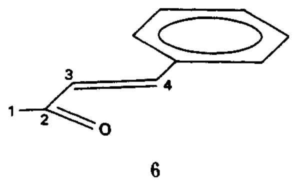

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Table I. Occupations of Benzylideneacetone π Orbitals

complex	occupation			
	π_1	π_2	π_3	π_4
Fe(CO)$_3$(bda)	1.952	1.919	1.101	0.040
Fe(CO)$_3$(PPh$_3$)(bda)	1.954	1.920	1.130	0.052

Fe(CO)$_2$L(bda) Complexes (L = CO, PH$_3$, P(OH)$_3$). Before trying to understand the bonding between bda and a Fe(CO)$_2$L fragment, we must choose the geometry of the resulting complex. The positions of the methyl and phenyl substituents were optimized by allowing them to rotate across the C–C bonds. The angle between the phenyl ring and the diene plane is 30.0°. The phosphine ligand is trans to the central C–C bond of the diene. This geometry was chosen after studying the energy changes occurring when the bda ligand is allowed to rotate around the z axis by 360°, as all the positions are different when L = PH$_3$ or P(OH)$_3$. The result is shown in Figure 4, for a series of complexes including the four species represented in 5 and coordinated respectively to Fe(CO)$_3$ or Fe(CO)$_2$(PH$_3$).

Let us now look only at the curves concerning bda. We will return to the others later. The three minima correspond to the three staggered conformations, which are different for Fe(CO)$_2$(PH$_3$)(bda), the deepest one having the phosphine trans to the midpoint of the central C–C bond of the diene. This result is in agreement with the experimental findings,[19-21] and the preference for the staggered conformations is again explained by the reasons outlined earlier.[24] On the other hand, the energy difference between the three minima is extremely small.

We can then take the staggered geometry for Fe(CO)$_3$(bda) in order to study its bonding. The left side of Figure 5 shows how the metallic fragment is bonded to bda. The strongest interaction is back-donation from the HOMO to the empty π_3 orbital of the enone (the overlap population between these orbitals is more than half the total overlap population between the two fragments). The diene donates electrons from π_1 and π_2 to empty orbitals of the Fe(CO)$_3$ fragment, 2e(a′) and 2a$_1$, π_2 being a better donor due to its higher energy, which is closer to that of the metallic fragment LUMO. The population of the diene orbitals is given in Table I, showing how π_3 is more than half-filled after binding to the metallic fragment, while π_2 and π_1 become partly depopulated.

This is a simplified picture of the bonding, as the symmetry of the complex is so low that all the orbitals can mix. As a conclusion, more electrons are donated than received by the metal. Looking at the composition of the diene orbitals, we can see that electron density is lost from oxygen (through π_1) and C$_3$ (large contribution to π_2, very small to π_3) and gained by C$_2$ (small contribution to π_2, medium to π_3) and C$_4$ (medium contribution to π_2, large to π_3). Essentially, oxygen can be considered the donor atom and C$_4$ the acceptor.

The general picture is kept when one of the carbonyls is replaced by the phosphine ligand (right side of Figure 5). Oxygen is still losing electrons to the metal fragment, while C$_4$ is receiving them. There is a small participation from the other two carbon atoms in the diene.

An important effect of the type of bonding, namely back-donation to π_3, is to increase the length of the central

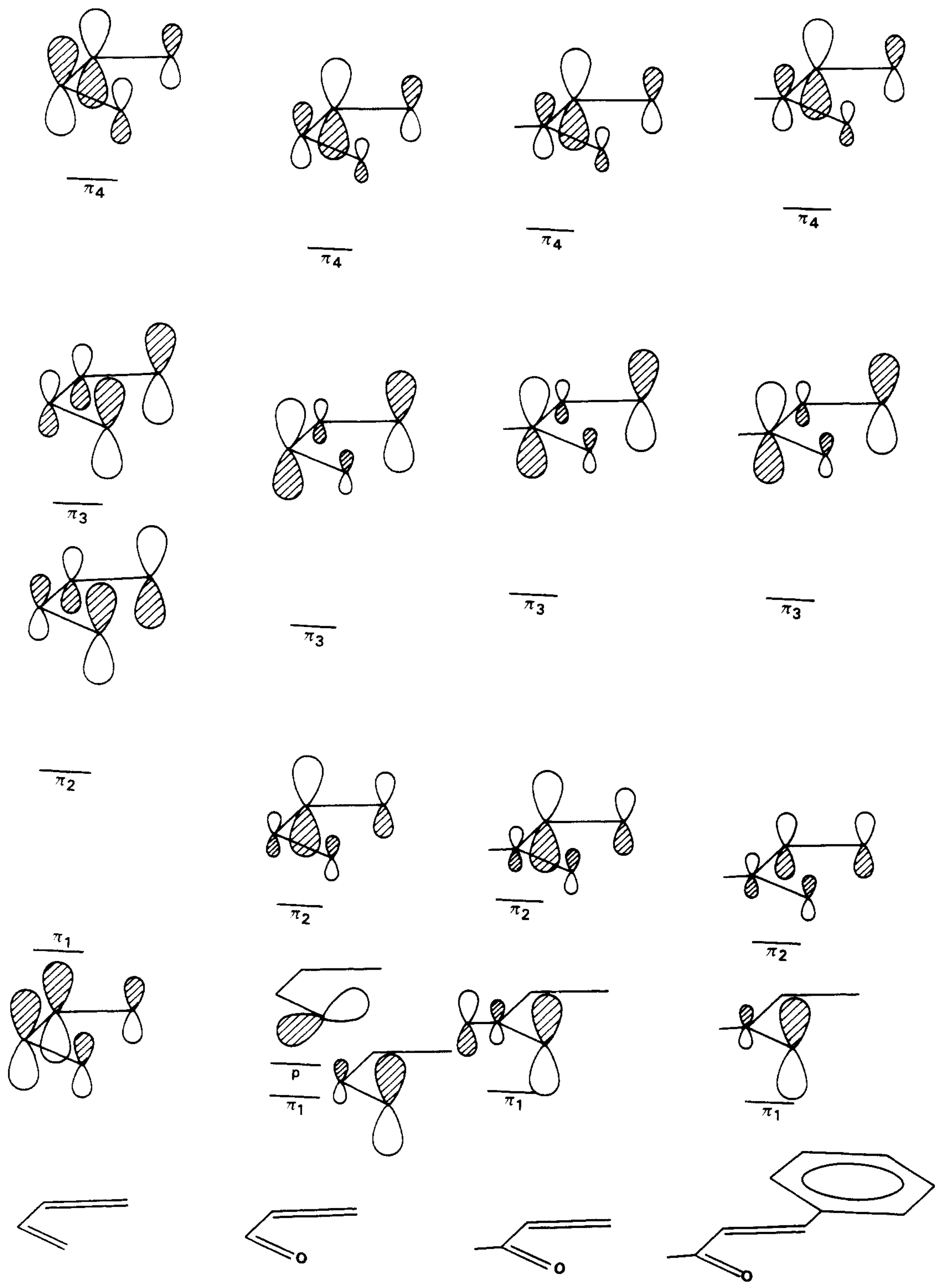
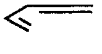
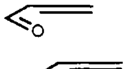
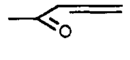


Figure 3. π orbitals of butadiene and some enones.

C_2–C_3 bond of the diene and decrease the terminal C_3–C_4 bond (**6**), as this orbital is bonding between C_2 and C_3 and antibonding between C_3 and C_4. This effect is reinforced by electron loss from π_2, which is bonding between C_3 and C_4 and antibonding between C_2 and C_3. This behavior is reflected by the overlap populations, which are shown in Table II (the bond lengths and angles used are the same for both the free and the coordinated ligands), and agrees with experimental values when available.[5,19]

Fluxional Behavior of the $Fe(CO)_2L(\eta^4$-enone) Complexes. We showed earlier (Figure 4) how the energy of $Fe(CO)_3(\eta^4$-enone) or $Fe(CO)_2(PH_3)(\eta^4$-enone) changed when the diene was allowed to rotate around the z axis. For the phosphine bda derivative, the global minimum is

Table II. C_3–C_4 (Terminal) and C_2–C_3 (Central) Overlap Populations in the Dienes

		overlap pop.		
ligand	bond	free ligand	$Fe(CO)_3L$	$Fe(CO)_2$-$(PH_3)L$
	C_3–C_4	1.177	0.995	0.992
	C_2–C_3	0.947	0.993	0.994
	C_3–C_4	1.129	0.991	0.988
	C_2–C_3	1.009	1.014	1.012
	C_3–C_4	1.142	0.986	0.989
	C_2–C_3	0.999	1.018	1.022
	C_3–C_4	1.103	0.989	0.987
	C_2–C_3	1.037	1.019	1.017

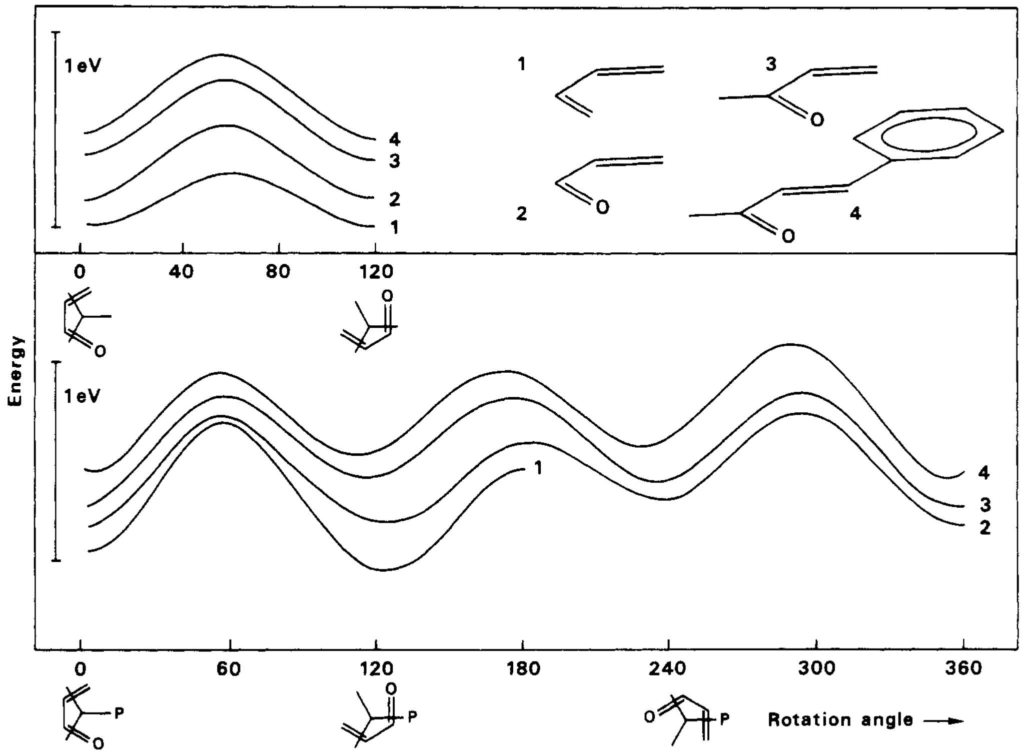


Figure 4. Change in total energy for rotation of a diene around the z axis in Fe(CO)$_3$(diene) (top) and in Fe(CO)$_2$L(diene) (bottom).

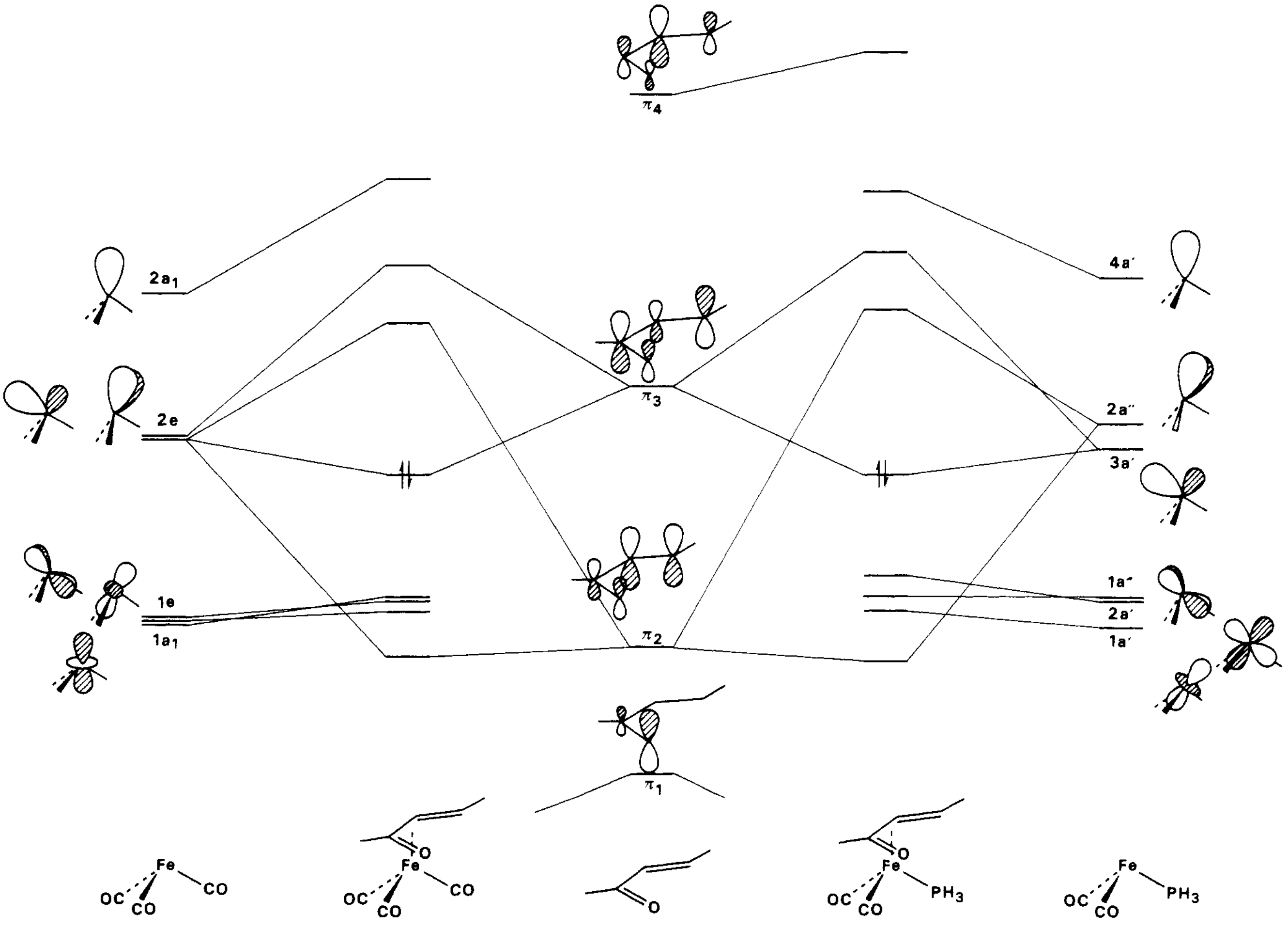
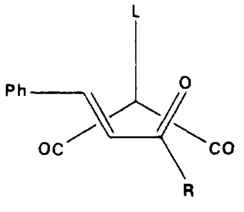


Figure 5. Interaction diagram between Fe(CO)$_3$ and bda (left side) and between Fe(CO)$_2$(PH$_3$) and bda (right side).

obtained when the enone is rotated 10° away from the staggered conformation, with the phosphine trans to the midpoint of C_2–C_3 (central bond), in good agreement with the experimentally determined structure.[19]

Many of these systems exhibit fluxional behavior in solution,[21,23,25,27] and at least two isomers are found in equilibrium. Although we wish to interpret these data, we cannot do it in detail using our previous results, as the bulk of the phosphines may be determining in the process and our model uses only PH_3. However, for this model, the barrier for bda rotation is calculated to be ca. 9 kcal mol^{-1} (L = CO) or ca. 12 kcal mol^{-1} (L = PH_3). Differences are very small if we try to compare this with other ligands, as Figure 4 shows.

Electronic vs Steric Factors in Determining the Isomer Distribution in $Fe(CO)_2L(\eta^4$-enone) Complexes. The balance of electronic/steric factors in determining the isomer distribution is apparent from a ^{31}P NMR study of $Fe(CO)_2L(\eta^4$-enone) complexes (enone = cinnamaldehyde, benzylideneacetone; L = phosphine, phosphite). These complexes exist in solution as interconverting mixtures of the isomers 7 and 8.[21] The nonoccurrence of the third possible isomer, 9, is probably due to the difficulty of removing the best π-acceptor CO ligand from the position trans to the oxygen atom, where the donor π_1 orbital of the enone is localized.



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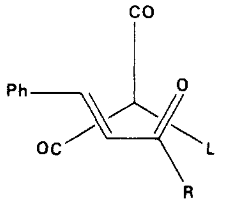

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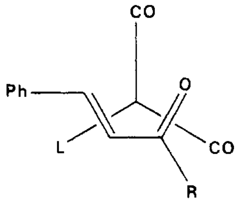

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In the cinnamaldehyde complexes (7, 8; R = H) the isomer ratio 7/8 increases in the order L = PPh_3 (0.6) < PPh_2Me (2.7) ≤ $PPhMe_2$ (2.8),[21] which is the order of increase of the σ-donor ability of the phosphine. In the benzylideneacetone complex (R = CH_3) the increase in the population of the isomer 7 (7/8 is 60 for L = PPh_3 and 86 for L = PPh_2Me) is probably due to a steric interaction between the phosphine and the methyl group in the isomer 8.[21] The results for both benzylideneacetone and cinnamaldehyde complexes, however, show that the 7/8 ratio is significantly higher for L = $PPhMe_2$ than for L = PPh_3, in spite of the former having a smaller cone angle (122 and 145°, respectively). This suggests that an electronic effect is also operating. The $PPhMe_2$ ligand being a better σ-donor than PPh_3 makes $Fe(CO)_2PPhMe_2$ a better electron donor than $Fe(CO)_2PPh_3$. This effect improves the overlap between the tilted orbitals of the $Fe(CO)_2L$ fragment and the enone orbitals, further stabilizing the staggered conformation with the phosphine trans to the midpoint of the central C_2–C_3 bond of the enone.

The operation of an electronic factor is also shown by a comparison between the $Fe(CO)_2L$(bda) complexes with L = $PPhMe_2$ and $P(OPh)_3$. In spite of both ligands having similar cone angles (122 and 128°, respectively), the $P(OPh)_3$ derivative shows a population of 8 ca. 4 times larger than that observed for the $PPhMe_2$ derivative, indicating that the better π-acceptor phosphite ligand can compete for the equatorial position with the CO ligand better than $PPhMe_2$.

Table III. Orbital Exponents and Parameters Used in the Extended Hückel Molecular Orbital Calculations

orbital	H_{ii}/eV	ζ_1	ζ_2	C_1	C_2
Fe 4s	−9.17	1.90			
Fe 4p	−5.37	1.90			
Fe 3d	−12.70	5.35	1.80	0.5366	0.6678

Electronic Effects in $Fe(CO)_2L$(bda) (L = CO, Phosphines, Phosphites) Studied by Carbon-13 Nuclear Magnetic Resonance. The calculations carried out in this work in general support the interpretation of the results of a ^{13}C NMR study of a series of $Fe(CO)_2L$(bda) complexes, with L = CO, phosphines, and phosphites.[20] The very large upfield shifts of the carbon atoms of bda involved in bonding with $Fe(CO)_2L$ were attributed to shielding by the electrons donated by this fragment. The shielding is bigger at the carbon atom C_4 (−80 to −96 ppm) than at C_2 (−53 to −55 ppm) or C_3 (−47 to −50 ppm). These carbon atoms have large, medium, or small contributions to the acceptor orbital π_3, respectively. The complex shift ΔC_4 of $Fe(CO)_3$(bda) (−81 ppm)[20] is larger than that of $Fe(CO)_3$(butadiene) (−75.5 ppm),[25] in agreement with our theoretical results, which show that bda is a better π acceptor than butadiene.

The complex shifts ΔC_4 of the phosphine and phosphite derivatives correlate well with the basicities of the phosphorus ligands estimated in terms of their ΔHNP values.[20] The complex shifts of the phosphite derivatives are larger than those expected on the basis of their ΔHNP values. The calculations with our model compounds show that the 3a′ orbital (HOMO) is more destabilized in the $Fe(CO)_2(P(OH)_3)$ fragment than in the $Fe(CO)_2(PH_3)$ fragment, implying that the former has a better donor capacity.

The very good correlation observed between the ratio $\Delta C_4/\Delta C_3$ and the Tolman electronic parameter, ν, of the phosphorus ligands[20] can be better understood in light of the present theoretical results. The parameter ν[26] is a measure of the relative ability of the $Fe(CO)_2L$ fragment in donating electrons. This ability depends on the combined σ-donor and π-acceptor properties. As the relative electron density at the iron atom in the $Fe(CO)_2L$ fragment increases, more electron density is transferred to the C_4 carbon atom, where the best acceptor orbital, π_3, is more localized. The electron density donated by the oxygen atom of bda to the metal fragment through π_1 is also partially transferred to π_3. The effect is larger for the phosphites compared to the phosphines. In agreement, the theoretical results showed the $Fe(CO)_2(P(OH)_3)$ fragment to be a better σ-donor and a better π-acceptor than $Fe(CO)_2(PH_3)$, as seen in Figure 2.

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Appendix

All calculations were of the extended Hückel type[22] with modified H_{ij}'s.[28] The basis set for the iron atom consisted of 4s, 4p, and 3d orbitals. The s and p orbitals were described by single Slater type wave functions, and d orbitals were taken as contracted linear combinations of two Slater wave functions. The geometries for the model complexes

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were taken from experimentally determined structures.[19] In the $Fe(CO)_2L$ fragment, the ligand–Fe–ligand angle was 90°. The plane of butadiene or the enone was 1.70 Å above the iron atom. Other distances used were the following (Å): Fe–C = 1.76; Fe–P = 2.23; C–O = 1.15; P–H = 1.42; P–O = 1.55; O–H = 1.00; C–C(diene) = 1.418; C–C(phenyl) = 1.39; C–H = 1.08 Å.

The parameters used for the calculations were the standard ones for C, H, O, and P and those reported on Table III for the iron atom.

Synthesis of Alkynylrhodium Complexes Containing a Rhodium–Mercury Bond and of the Vinyl Complex $[C_5H_5Rh(CH{=}CHPh)(P\text{-}i\text{-}Pr_3)SnCl_3]$ from Vinylidenerhodium Precursors[1]

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The reaction of $[C_5H_5Rh({=}C{=}CHR)(P\text{-}i\text{-}Pr_3)]$ (**1–3**) with $HgCl_2$, HgI_2, and CH_3HgI in presence of triethylamine produces the alkynylrhodium complexes $[C_5H_5RhHgX(C{\equiv}CR)(P\text{-}i\text{-}Pr_3)]$ (**4**, **6–11**) in excellent yield. They have been characterized by ^1H, ^{13}C, ^{31}P, and ^{199}Hg NMR spectroscopy. Treatment of **1** (R = Ph) with $SnCl_2{\cdot}2H_2O$ gives the vinylrhodium compound $[C_5H_5Rh(CH{=}CHPh)(P\text{-}i\text{-}Pr_3)SnCl_3]$ (**12**) probably via primary protonation at the metal atom. Complex **12** is also obtained from $[C_5H_5Rh(CH{=}CHPh)(P\text{-}i\text{-}Pr_3)Cl]$ and $SnCl_2{\cdot}2H_2O$ by insertion of tin dichloride into the Rh–Cl bond.

Introduction

The vinylidenerhodium complexes $C_5H_5Rh({=}C{=}CHR)(PR'_3)$ belong to the family of half-sandwich type compounds C_5H_5MLL', which provided that at least one of the ligands L and L′ possesses good donor properties are strong nucleophiles, i.e., metal bases.[2,3] Recently, we have already demonstrated that the vinylidene compounds $C_5H_5Rh({=}C{=}CHR)(P\text{-}i\text{-}Pr_3)$ (R = H, Me, *t*-Bu, Ph) react with Brønsted acids HX to form substituted vinylrhodium complexes $C_5H_5Rh(CH{=}CHR)(P\text{-}i\text{-}Pr_3)X$ (X = Cl, I, CF_3CO_2) probably via attack of the acid at the metal center.[1,4] Other electrophiles such as diazomethane, sulfur, selenium, tellurium, CuCl, $[Fe(CO)_4]$, etc., behave similarly.[1,5-7]

Owing to our long-standing interest in using the rhodium derivatives C_5H_5RhLL' also as starting materials for the preparation of metal–metal bonded complexes,[8] we became interested in exploring the reactivity of $C_5H_5Rh({=}C{=}CHR)(P\text{-}i\text{-}Pr_3)$ toward mercury dihalides and related species. We note that the first evidence for the interaction between a half-sandwich complex $C_5H_5ML_2$ and an electrophile came from the work by Kemmitt et al.,[9] who showed that on treatment of $C_5H_5Co(CO)_2$ with HgX_2 (X = Cl, Br, I) 1:1 adducts are formed. It was proved by the X-ray structural analysis of $[C_5H_5Co(CO)_2HgCl_2]$ that these nonionic substances contain a direct metal–metal bond.[10] Analogous 1:1 adducts have also been obtained from $C_5H_5Rh(CO)_2$ or $C_5H_5M(diene)$ (M = Co, Rh; diene = norbornadiene, cycloocta-1,5-diene) and $HgCl_2$,[9,11] as well as from $C_5H_5RhL_2$ (L = PMe_3, PMe_2Ph, PEt_3) and $AlMe_3$.[12]

We report in this paper that a similar interaction probably takes place between $C_5H_5Rh({=}C{=}CHR)(P\text{-}i\text{-}Pr_3)$ and HgX_2 or CH_3HgI, respectively. The electrophilic addition is rapidly followed by HX elimination, which results in the formation of novel alkynylrhodium complexes having a Rh–Hg bond.

Results

Reaction of **1** with $HgCl_2$ in benzene or THF leads spontaneously to the formation of a deeply colored solution from which approximately equal amounts of **4** and **5** can be isolated (Scheme I). If the benzene solution of **1** is first treated with excess triethylamine and then with $HgCl_2$, the alkynyl complex **4** is obtained in virtually quantitative yield. The amine method also works with **2** and **3** as starting materials and $HgCl_2$, HgI_2, and CH_3HgI as substrates to give **6–11** again nearly quantitatively. The Rh–Hg compounds are orange to red–brown microcrystalline solids that for short times can be handled in air. The solubility in ether and hydrocarbon solvents increases in the order R = Ph < Me < *t*-Bu and also from the mercury chlorides to the iodides. Only the complex **11**, which is

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