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ν(M-M) Spectra of $H_4M_4(CO)_{12}$ (M = Ru, Os) and $H_2Ru_4(CO)_{13}$

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The "plastic cluster" model, in which a complete but approximate G matrix is used but the F matrix is diagonal, provides a good description of the ν(M-M) spectra of the title compounds.

In recent years there have been extensive advances in the preparative and structural characterization of metal cluster compounds. In contrast, relatively little progress has been made in the study of the vibrational properties of these species. The characteristics of specific cluster-bonded ligands—often simple hydrocarbons—have provided insights into the chemical identity of molecular fragments coordinated to single-crystal metal surfaces and studied by EELS,[1] but the clusters themselves have been little studied. Where detailed analyses have been made, they were of the ν(CO) vibrations of high-symmetry molecules—$M_4(CO)_{12}$ (T_d)[2] and $M_3(CO)_{12}$ (D_{3h})[3]—although less detailed work has revealed interesting and potentially useful structure–spectra relationships in the metal–metal vibrations of triangular M_3 systems of C_{2v} symmetry.[4] It seems clear that the pattern of metal–metal vibrations is rather sensitive to molecular geometry—indeed, the simplest model used in the interpretation of these vibrations requires a complete G matrix but only a diagonal F matrix.[5] Against this must be set three difficulties. First, it has been recognized that geometrical distortions may have only a second-order effect on frequencies (and, in particular, the relief of degeneracies). Physically, this situation arises when the "distorted" and "undistorted" internal coordinates are inseparable—when it is only possible to designate symmetry coordinates in which both "distorted" and "undistorted" appear in all symmetry coordinates. Although such cases exist, and have been discussed, they occur in a limited set of geometries.[6] Second, metal–metal stretching vibrations occur at frequencies little above those associated with other low-frequency motions, such as δ(M–M–X). Although there is no evidence that mixing between ν(M–M) and such deformations is important, their occurrence in proximate frequency regions poses problems for band assignments. Isotopic data would help overcome some of these problems; alternatively, it may be that band intensities and patterns sometimes provide guidance. Failing all else, some reasonable physical model may be of value. Third, an isolated M–M stretch is not dipole-active; it follows that combinations of such stretches are unlikely to lead to strong infrared bands. However, as we shall see, the dipole activity can be of vital importance in band assignments. In contrast, M–M stretches are expected to show strong Raman activity, and not surprisingly, Raman data dominate the literature in this subject area.

In this paper we report our studies of the ν(M–M) spectra of three M_4 species, two of which ($H_4Ru_4(CO)_{12}$ and $H_4Os_4(CO)_{12}$) have D_{2d} molecular symmetry.[7,8] For these, the M_4 framework is approximately tetrahedral; the distortion to D_{2d} is expected to produce a first-order splitting of vibrations degenerate in T_d. Although the third compound on which we report, $H_2Ru_4(CO)_{13}$ has a structure in which the arrangement of metal atoms is also derived from a tetrahedron, the overall symmetry is C_s.[9] The two shortest bonds are C═O bridged; the two longests are H bridged.

For an M_4 system of T_d symmetry the six ν(M–M) vibrations fall into three sets, all Raman active. In order of descending frequency these are A_1, the strongest band of the set, and T_2 E, both of which have considerabe intensity. In the "plastic cluster" model the ratios $\nu(A_1)/\nu(T_2)$ and $\nu(T_2)/\nu(E)$ are both predicted to be 1.41.[5] The frequency ratios actually observed, while approximating to the predicted values, tend to be somewhat smaller; in $Ir_4(CO)_{12}$ the actual ratios found are 1.29 and 1.23, respectively.[5]

On descent to D_{2d} symmetry the T_2 mode is expected to split into two bands (B + E (D_{2d}) of a 2:1 intensity ratio in both Raman and infrared spectra) while the E(T_d) mode is expected to split into two ($A_1(T_d)$ + B_1) of equal intensity in the Raman spectra. These intensity predictions are only approximate, but they are a potentially useful guide since they may enable a check on the expected frequency order $A_1 > T_2 > E$ (all T_d).

The symmetry of $H_2Ru_4(CO)_{13}$ is only C_s, so that all degeneracies may be lifted. In practice, however, this molecule follows the pattern of those of D_{2d} symmetry, no additional relief of degeneracy being evident. It is for this reason that it is included in this paper.

As indicated above, the possible overlap between ν(M–M) and δ(M–M–C)/δ(C–M–C) frequencies is a potential problem in the present work. It will be helpful toward a resolution of this problem to reconsider the δ(M–M–C)/δ(C–M–C) modes of $Ir_4(CO)_{12}$ from a viewpoint somewhat different from that adopted in the literature.[5] We have elsewhere argued that such modes may be derived from modes associated with individual metal atoms.[10] In the present case this means that we consider the deformation motions of an IrC_3 (actually, $Ir(C–O)_3$) unit, the Ir atom being part of an Ir_4 tetrahedron (so that some of the motions of carbon atoms result in changes in M–M–C bond angles). We now allow each carbon atom two motional degrees of freedom perpendicular to the corresponding Ir–C bond. Such motions may be conveniently distinguished by their behavior with respect to reflection in the local mirror plane as radial (symmetric) and equatorial (antisymmetric). The labels "radial" and "equatorial" describe the motional degrees of freedom viewed down the threefold axis. The three radial motions transform as A_1 + E in the local C_{3v} symmetry; the three equatorial motions transform as A_2 and E. Of these, A_2 is infrared- and Raman-silent, while A_1 and E modes are active in both. A total of three Raman features is predicted for an isolated IrC_3 unit.

The local modes on the four Ir atoms are weakly coupled in $Ir_4(CO)_{12}$; the molecular species arising are as follows:

C_{3v}		T_d
A_1	→	$\underline{A_1} + \underline{T_2}$
A_2	→	$A_2 + T_1$
E	→	$\underline{E} + T_1 + \underline{T_2}$ (note: E(C_{3v}) appears twice)

Those species Raman-active in T_d are underlined. This pres-

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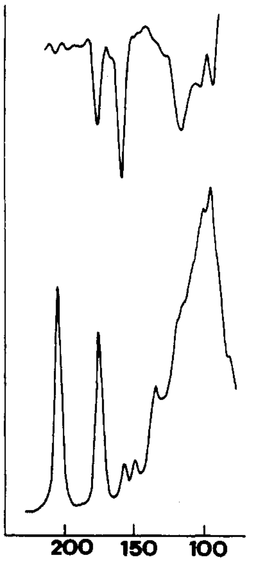

Figure 1. (a) Infrared (upper) and (b) Raman spectra of crystalline $H_4Ru_4(CO)_{12}$ in the ν(Ru–Ru) region.

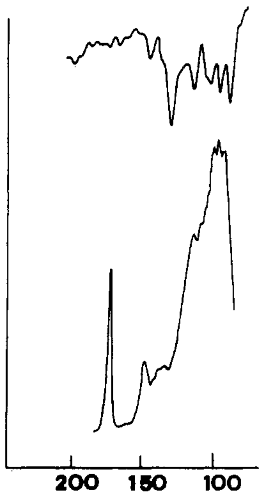

Figure 2. (a) Infrared (upper) and Raman (b) spectra of crystalline $H_4Os_4(CO)_{12}$ in the ν(Os–Os) region.

entation makes clear the origin of Quicksall and Spiros' statement in the context of Raman bands: "the six bending modes are always calculated as three closely spaced pairs"[5]—the coupling between deformations associated with a single metal atom (the central atom in these deformations) is greater than those between deformations associated with different metal atoms. It follows, then, that we may expect a similarity between the δ(C–M–C)/δ(M–M–C) features in $Ir_4(CO)_{12}$ and our $H_4M_4(CO)_{12}$ compounds—since local couplings dominate, the spectral features are expected to display an element of insensitivity to small changes in the M_4 framework. It is not to be expected that the spectral features are superimposable—the detailed geometry at individual metal atoms is not constant—but, rather, that the spectral region covered by these modes and the general distribution of band intensity is likely to be similar. $H_2Ru_4(CO)_{13}$ may be somewhat different. It contains three $Ru(CO)_3$ groups and one $Ru(CO)_2$—we ignore bridging carbonyls for the moment. In that the model we invoke is, to first approximation, an additive one (if the coupling between $M(CO)_3$ units were zero, it would be accurately additive), we may expect the three $Ru(CO)_3$ groups to dominate and the ~100-cm^{-1} region in the Raman spectrum of this compound to be not too different from those of the other three compounds. That this expectation is justified is evident from our spectra (Figures 1–3) and that of $Ir_4(CO)_{12}$, which is available in the literature.[5] In all, there is a strong peak at ~100 cm^{-1} with some fine structure, the details of which differ.

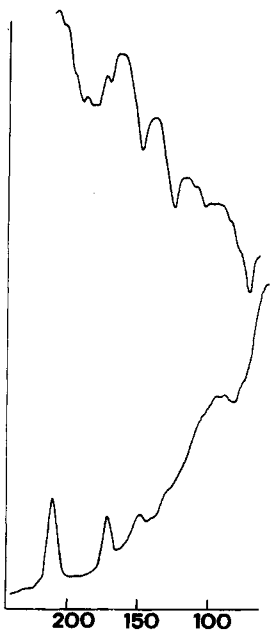

Figure 3. (a) Infrared (upper) and (b) Raman spectra of crystalline $H_2Ru_4(CO)_{13}$ in the ν(Ru–Ru) region.

Results and Discussion

In complicated systems such as those we consider in the present work it is easy to invoke underdetermined models. Is it to avoid this problem that we work with the simplest possible model and do not attempt to quantitatively include the deformation modes that lie at the lower end of the frequency range under study.

In a distortion from T_d to D_{2d} of a metal tetrahedron, it is necessary in the simple plastic cluster model to work with two ν(M–M) force constants, corresponding to the two different M–M bond lengths.[5] All other electronic, bonding, changes are irrelevant because of the neglect of interaction force constants. On the other hand, the distortion from T_d to D_{2d} is accurately described by the modified **G** matrix. It is therefore reasonable to expect that the accuracy of the simple plastic cluster model should be comparable in both T_d and D_{2d} geometries. If this expectation is correct, it may well be possible to use the model in low-symmetry systems. In this paper we report a study of the applicability of the plastic cluster model to such low-symmetry systems. To test its utility when applied to molecules of symmetry as low as C_s, we also include $H_2Ru_4(CO)_{13}$, although, as we have already commented, its ν(M–M) spectra are not evidently different from those of the D_{2d} species. In the (diagonal) force constant matrix, it is necessary to recognize two different force constants, that corresponding to the short metal–metal bonds (f_s) and that corresponding to the long (f_l). The best-fit values obtained (M = Ru $f_s = 0.8, f_l = 0.6$; M = Os $f_s = 1.2, f_l = 1.0$) are in accord with the conclusion that Os–Os bonds are stronger than their Ru–Ru counterparts and that the presence of bridging H atoms weaken the direct M–M bonding by removing electron density from the M–M bond.

The clearest spectra are those of $H_4Ru_4(CO)_{12}$ (those of the deuterio compound are essentially superimposable and so not included here). We therefore discuss these spectra in some detail and refer the spectra of other compounds to them. Raman spectra are given in Figures 1a–3a, and frequency data are collected in Table I. The Raman spectrum of $H_4Ru_4(CO)_{12}$ shows the expected five peaks in the 200–120-cm^{-1} region. Of these, the highest frequency and greatest intensity undoubtedly belong to the A_1 peak. However, no pair of peaks shows the 2:1 intensity ratio expected for the split T_2 mode (T_2 in T_d becomes B_2 + E in D_{2d}). There is, then, no applicable Raman intensity criterion that distinguishes between several alternative assignments of the Raman spectrum, although the insertion of reasonable force constant values together with the observed geometry into the plastic cluster model (Appendix) leads to the predition that $\nu(B_2) > \nu(E)$. This prediction is confirmed by the infrared spectrum. Only T_2 modes

Table I. ν(M–M) Frequencies (cm^{-1})

		$H_4Ru_4(CO)_{12}$		$H_4Os_4(CO)_{12}$		$H_2Ru_4(CO)_{13}$	
C_{3v}	D_{2d}	T_d	IR	Raman	IR	Raman	IR
	A_1	199		172		213	
T_2	B_2	170	171	147	146	174	174
	E	153	154	~136	130	~150?	150
E	A_1	146		~133		~150?	
	B_1	131		~114		~134? (125?)	
"T_d"	$\nu(A_1)/\nu(T_2)$	1.25 (1.27)[a]		1.23 (1.24)[a]		1.35	
	$\nu(T_2)/\nu(E)$	1.14		1.13		1.11 (1.15)	

[a] Assignment II; see Table II.

Table II

$H_4Ru_4(CO)_{12}$

	alternative assignts		
freq, cm^{-1}	I	II	best fit for f_1 = 0.6, f_s = 0.8
199 s	A_1	A_1	A_1 212
170 s	B_2	B_2	B_2 164
153 w	E	}E	E 142
146 w	A_1		
131 m	B_1	A_1	A_1 115 B_1 96

$H_4Os_4(CO)_{12}$

	alternative assignts		
freq, cm^{-1}	I	II	best fit for f_1 = 1.0, f_s = 1.2
172 s	A_1	A_1	A_1 190
147 s	B_2	B_2	B_2 143
136 w, br	E	}E	E 130
133 w, br	A_1		
114 m	B_1	A_1	A_1 103 B_1 90

in T_d are infrared-active and only B_2 and E in D_{2d}. Two bands, coincident with two in the Raman spectrum to within error, are observed (Figure 1b) and have the anticipated 1:2 (B_2:E) intensity ratio. By exclusion, the two remaining Raman peaks, of comparable intensity, are most probably to be assigned as components of the split E(T_d) mode. Because it is indicated by the plastic cluster model (Appendix), we assign the higher frequency as A_1 and the lower as B_1. Unfortunately, we have not been able to obtain Raman spectra of a solution because of the low solubility of the compound in common solvents, which, through a measurement of polarization ratios, might enable a check on this assignment. It is to be recognized that a viable alternative exists. The peaks assigned as E(D_{2d}) and lower A_1(D_{2d}) could, in fact, be the components of the E(T_d) mode (which, in this alternative, is split). In this case, the lowest observed frequency becomes the A_1. This latter model enables a better fit to be obtained with a normal-coordinate analysis but is not in such good accord with the observed Raman intensities. The two assignments are compared in Table II.

One problem remains, in both of the models presented above: that of the surprisingly high Raman intensity of the B_2 mode, relative to that of the E. Although alternative explanations exist, the most probable lies in the crystal structure.[7] In the crystal the $H_4Ru_4(CO)_{12}$ molecules are arranged such that there is nearly a threefold crystallographic axis (if it actually existed, the space group would be *P*31*m*, not *P*1). Each molecule is, then, subject to an intermolecular potential which is approximately symmetrical about a threefold axis of the parent M_4 tetrahedron. However, the intramolecular potential is symmetrical about a twofold axis of this tetrahedron (the *z* axis in D_{2d} symmetry). This conflict of potentials is manifest in the molecular site symmetry, which is C_1. We believe that this low-symmetry component causes some mixing between the adjacent $\nu(B_2)$ and $\nu(A_1)$ modes, leading to intensity enhancement of the former. It has been commented elsewhere that intensity stealing is often more evident in the Raman than in the infrared[11] spectra (there is evidence of weak infrared intensity in the $\nu(A_1)$ mode but nothing as strong as in the Raman spectra; it will be seen that we have not included it in Table I). Further, intensities are usually more sensitive to mixing than are frequencies; so, it is our experience that, for instance, the components of an E mode split by a few cm^{-1} may have relative intensities differing by a factor of 3; perhaps this is why the ν(E)(D_{2d}) mode shows no sign of splitting. If our explanation of the Raman intensity of $\nu(B_2)$ is correct, the intensity should become "normal" in a solution Raman spectrum. Unfortunately, as indicated earlier, we have been unable to obtain this spectrum.

The assignment of the ν(M–M) frequencies of $H_4Os_4(CO)_{12}$ (Figure 2) and $H_2Ru_4(CO)_{13}$ (Figure 3) follow those of $H_4Ru_4(CO)_{12}$. Both $H_4Os_4(CO)_{12}$ and $H_4Ru_4(CO)_{12}$ contain disorder in their lattices, that for the osmium compound involving about 5% of the molecules compared with 3% in the ruthenium species. This may be why the B_2 and E(D_{2d}) ν(M–M) peaks for the osmium compound are significantly broader than those for the ruthenium. A comparison of the infrared and Raman spectra of the osmium compound suggests that the lower frequency A_1 ν(M–M) mode may be at marginally higher frequency than the E; certainly, it is not possible to distinguish two peaks in the Raman spectrum in this region. Broadening also seems to affect the lowest frequency, B_1, band, which seems to be present as a barely discernible shoulder on the δ(C–M–C)/δ(M–M–C) feature. In that the splittings of the T_2(T_d) and E(T_d) modes are comparable for $H_4Ru_4(CO)_{12}$ (16 and 15 cm^{-1}, respectively), we would expect a similar pattern for the isostructural $H_4Os_4(CO)_{12}$. This comparability is contained within the above assignment. Because a peak at 112 cm^{-1} for $H_4Ru_4(CO)_{12}$ is assigned as a deformation feature, so too is that at 114 cm^{-1} for the osmium compound (vide supra).

In $H_2Ru_4(CO)_{13}$, as befits its lower symmetry, the splitting on the T_2(T_d) mode is the greatest of all those we report (24 cm^{-1}). The lowest, B_1, mode is difficult to assign because of the proximate deformation peak in the Raman spectrum. The nearest shoulder is at 135 cm^{-1}, but if the splittings of T_2(T_d) and E(T_d) are again comparable, a shoulder at 127 cm^{-1} may be preferable.

Although minor ambiguities of assignment remain, they do not affect the major conclusion of the present work. This is that, as evident from the bottom lines of Table I, whereas the $\nu(A_1)/\nu(T_2)$ ratios for all of the compounds we report are similar to that for $Ir_4(CO)_{12}$ (where the ratio is 1.29), the $\nu(T_2)/\nu(E)$ ratios are markedly inferior to that for $Ir_4(CO)_{12}$ (for which it is 1.23). The breakdown of the model, then, largely occurs because of the frequencies assigned to the A_1 and B_1 components of the E(T_d) vibration. This may indicate either a weakness in the plastic cluster model (we note that assignment II in Table II is marginally closer in accord with the plastic cluster model than is assignment I), or a mixing between ν(M–M) and the deformation vibrators. Quicksall and Spiro found such mixing in $Ir_4(CO)_{12}$, but it occurred to only a small extent. In the present case this mixing will surely be greatest for the E(T_d) region. If this latter explanation

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(11) These Raman spectra of the $H_4M_4(CO)_{12}$ compounds have previously been reported by: Marzocchi, M. P.; Angeloin, L.; Benedetti, E.; Bianchi, M.; Frediani, P. *Indian J. Pure Appl. Phys.* **1978**, *16*, 304.

is correct, then a study of the ^{13}CO species should lead to data in better agreement with the plastic cluster model.

The final question to be considered is whether a simple modification of the plastic cluster model enables a better fit to the data. We have considered several models of which we detail two as examples (Appendix). In one of these we introduce an interaction force constant between the long and short M–M bonds, and in the other we introduce it between the long bonds. As expected, the introduction of a further variable gives a better fit between the data and theory but the physical meaning of the improvement is unclear—thus, either of the two modifications enable the ratio of A_1 frequencies to be varied. Rather, we prefer to work with the simple plastic cluster model, for it predicts a frequency order that is in accord with all experimental data and gives predicted bond angles (using the expression for cos β given in the Appendix) that are in tolerable accord with the experimental values. Almost certainly a major error is the neglect of mixing of ν(M–M) with deformation modes, and this neglect is not adequately compensated by the introduction of ν(M–M) interaction constants in the simple model.

There remain two aspects of the vibrational spectra of $H_2Ru_4(CO)_{13}$ (Figure 3) that merit comment. First, it is the only species to show a strong Raman band that overlaps with the lower frequency end of the region assigned to δ(C–M–C)/δ(M–M–C), although the other compounds appear to have a similar band at much lower frequencies. It may be that this band is to be assigned to lattice translatory modes. Some of the translation vibrations of a cluster of isotropic, uncharged spherical molecules would be expected to show strong Raman activity because they correspond to changes in shape or orientation of the corporate polarizability ellipsoid. Such motions would normally be at low frequency (their acoustic counterparts have zero frequency at $k = 0$), but for rather irregular molecules supporting an inherent dipole, some considerably frequency increase is possible.

The second point worthy of comment is the rather broad infrared band centered at ~185 cm^{-1}, which is without counterpart in any of the other spectra. In that we are confident that it is not due to an impurity, we incline to assign it to δ(M–M–C) modes involving the bridge carbonyls, which must surely lie at a higher frequency than those of terminal carbonyl groups. If this assignment is correct, the absence of Raman activity on these vibrations is to be noted.

Experimental Section

$H_4Ru_4(CO)_{12}$[12] and $H_2Ru_4(CO)_{13}$[13] were prepared according to the literature methods. $H_4Os_4(CO)_{12}$ was kindly supplied by Dr. B. F. G. Johnson (Cambridge).

The Raman spectra were recorded on a Spex Raman spectrophotometer, Model 1401, equipped with a Spectra Physics Model 165 mixed-gas laser (exciting line 6471 Å) with incident power of ~25 mW. Very slow scanning enabled a resolution of ~4 cm^{-1}. The IR spectra in the 400–20 cm^{-1} region were obtained by a Beckman RIIC IR720M interferometer, the samples being dispersed in pressed polyethene plates.

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Appendix

The plastic cluster model requires a complete **G** matrix and a diagonal **F** matrix in which two M–M stretching force constants are included, one referring to the long H-bridged M–M bonds (f_l) and one to the short nonbridged M–M bonds (f_s). The following equations are easily obtained:

$$\nu_1(A_1) = [(1 + \cos\beta)f_l + f_s + \Delta]^{1/2} \qquad (1)$$

$$\nu_2(A_1) = [(1 + \cos\beta)f_l + f_s - \Delta]^{1/2} \qquad (2)$$

$$\nu_3(B_1) = [2(1 - \cos\beta)f_l]^{1/2} \qquad (3)$$

$$\nu_4(B_2) = [2f_s]^{1/2} \qquad (4)$$

$$\nu_5(E) = [2f_l]^{1/2} \qquad (5)$$

where $\Delta^2 = [(1 + \cos\beta)f_l + f_s]^2 - 8(\cos\beta)f_lf_s$ and β is the angle between the long M–M bonds.

From eq 1–4, β can be obtained as

$$\cos\beta = (\nu_1^2 + \nu_2^2 - \nu_3^2 - \nu_4^2)/(\nu_1^2 + \nu_2^2 + \nu_3^2 - \nu_4^2)$$

Assuming, reasonably, that $f_l < f_s < 2f_l$ and $\beta = 60 \pm 5°$, we find

$$\nu_1 \sim 2\nu_2 \qquad \nu_4 > \nu_5 > \nu_3$$

The introduction of interaction constants between the stretching of two adjacent M–M bonds gives rise to the following modifications:

(a) f_{ls} (coupling between long and short bonds)

$$\nu_1 = [(1 + \cos\beta)f_l + f_s + 4(2^{1/2})(1 - \cos\beta)^{1/2}f_{ls} + \Delta']^{1/2}$$

$$\nu_2 = [(1 + \cos\beta)f_l + f_s + 4(2^{1/2})(1 - \cos\beta)^{1/2}f_{ls} - \Delta']^{1/2}$$

where $\Delta' = [(1 + \cos\beta)f_l + f_s]^2 - 8\ (\cos\beta)(f_lf_s - 8f_{ls}^2)]^{1/2}$.

(b) f_{ll} (coupling between two long bonds)

$$\nu_1 = [(1 + \cos\beta)(f_l + 2f_{ll}) + f_s + \Delta'']^{1/2}$$

$$\nu_2 = [(1 + \cos\beta)(f_l + 2f_{ll}) + f_s - \Delta'']^{1/2}$$

$$\nu_3 = [2(1 - \cos\beta)(f_l - 2f_{ll})]^{1/2}$$

where $\Delta'' = [(1 + \cos\beta)(f_l + 2f_{ll}) - 8(\cos\beta)f_s(f_l + 2f_{ll})]^{1/2}$.

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Notes

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Formation of a Nickel Carbonyl Cation Containing a Cyclophosphenium Ligand by Hydride Abstraction

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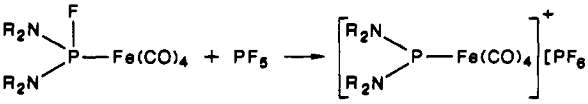
Following the discovery of the first cyclophosphenium cation by Fleming[1] and co-workers, the first metal carbonyl containing a phosphenium cation as a ligand was obtained in this laboratory[2] by direct reaction of the cyclic phosphenium cation with $Fe(CO)_5$ or $Fe_2(CO)_9$. A more effective route to these metal complex cations was found[2] to be halide extraction using a strong Lewis acid as a halide ion acceptor. A typical reaction involving fluoride ion removal is given by



(1)

Muetterties and co-workers[3] were able to extract an OR$^-$ group

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