

error estimate cannot be provided. Activation volumes reported for the pyrdtc complex are those calculated at room (or effectively zero) pressure; since data were collected at five pressures up to 1380 bar in each solvent, accurate error estimates were obtained.

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UV Photoelectron Spectroscopic Studies of the Metal-Olefin Bond. 2. Bonding in (β -Diketonato)rhodium(I) and -iridium(I) Carbonyl and Olefin Complexes¹

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The He I and He II photoelectron spectra of series of (β -diketonate)ML₂ complexes (β -diketonate = enolate anion of 2,4-pentanedione, 2,2,6,6-tetramethyl-3,5-heptanedione, 1,1,1-trifluoro-2,4-pentanedione, or 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, M = Rh or Ir, L = CO, ethylene, or propylene) are reported. Assignments are proposed, on the basis of He I/He II intensity differences, on MO calculations, on related complexes, and on empirical comparisons. The electronic structure of the complexes is discussed, and conclusions can be drawn about the trends in σ donation and π back-donation in the metal-olefin bond in the various complexes.

Introduction

As an extension of previous investigations in our laboratory of metal-olefin complexes,²⁻⁴ we studied a series of Rh and Ir olefin complexes with UV photoelectron spectroscopy (UPS). These complexes have already been the subject of thermochemical, IR/Raman, and NMR investigations.⁵

Thorough studies of the He I spectra of a large number of β -diketonate transition-metal complexes have been reported,⁶⁻⁹ but information about the monovalent rhodium and iridium β -diketonate dicarbonyl and diolefin complexes is lacking. In fact, to our knowledge, no gas-phase UPS data of square-planar Ir(I) and Rh(I) complexes have been published.

We now report the He I and He II photoelectron spectra of a series of LMX₂ complexes, where L is the enolate anion of a β -diketonate [2,4-pentanedione, commonly known as acetylacetonate (acac), 1,1,1-trifluoro-2,4-pentanedione (tfa), 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfa), or 2,2,6,6-tetramethyl-3,5-heptanedione (tmh)], M = Rh or Ir, and X = CO, ethylene, or propylene. The structures of the complexes are shown in Figure 1. All complexes under study here are assumed to have C_{2v} symmetry, except of course the complexes with the asymmetric tfa ligand and the propylene complexes which can exist as many isomers.⁵ All the complexes are square planar coordinated while the olefins are perpendicular to the molecular plane.

The aim of this investigation is to extend our knowledge of the nature of the metal-olefin bond and in particular to in-

vestigate the influence exerted on this bond by variation of the β -diketonate ligand and substitution of the olefin. The assignments are made by using He I/He II cross-section variations and by using some results of extended CNDO calculations on model cobalt complexes.

Experimental Section

Synthesis. The complexes were prepared according to the literature.^{5,10,11} They were purified by recrystallization and vacuum sublimation, and their purity was checked by elementary analysis, ¹H NMR, and IR. Jesse⁵ studied the behavior of these complexes upon heating in vacuo in a Mettler Type 1 thermoanalyzer and found no decomposition.

We failed to record PE spectra of a series of complexes in which the β -diketonate is 1,3-diphenyl-1,3-propanedione. These complexes have almost no vapor pressure, and decomposition occurred upon heating. Decomposition also occurred in complexes in which the olefin was varied to methyl acrylate, vinyl chloride, styrene, and vinyl acetate.

Photoelectron Spectra. The spectra were recorded on a Perkin-Elmer PS 18 photoelectron spectrometer modified with a Helictros He I/He II source. The spectra were calibrated with respect to Ar and Xe lines as internal calibrants. Due to strongly overlapping bands in the spectra, so that no accurate deconvolution of the peaks could be achieved, the intensity arguments used as an assignment criterion are based on spectra uncorrected for analyzer dependence.

Results

In order to assign the spectra we require a molecular orbital scheme for these molecules. Extended CNDO calculations¹² have been performed on two model systems [acacCo(CO)₂] and [acacCo(C₂H₄)₂].¹³ These calculations gave some indication of the character and the relative ordering of the molecular orbitals, and these results were used in the assign-

- (1) For part 1 see ref 2b.
- (2) (a) Baerends, E. J.; Oudshoorn, C.; Oskam, A. *J. Electron Spectrosc. Relat. Phenom.* **1975**, *6*, 259. (b) van Dam, H.; Oskam, A. *Ibid.* **1979**, *16*, 307.
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- (11) van Gaal, H. L. M.; van der Ent, A. *Inorg. Chim. Acta* **1973**, *7*, 653.
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- (14) Bailey, N. A.; Coates, E.; Robertson, G. B.; Bonati, F.; Ugo, R. *Chem. Commun.* **1967**, 1041 and references therein.

Table I. Vertical Ionization Energies of (β -diketonato)RhL₂ (L = CO, C₂H₄, C₃H₆) Complexes^{a, b}

	metal d orbitals			β -diketonate orbitals			
	14a ₁ , 5b ₂	13a ₁ , 4a ₂		4b ₁ (π_3)	11b ₂ (n ₋)	12a ₁ (n ₊)	
tmhRh(CO) ₂	8.3	(9.4)			9.4	(10.8)	
acacRh(CO) ₂	8.5	(9.5)		(9.8)	10.0	11.2	
tfaRh(CO) ₂	9.0	(9.6)			10.5	11.7	

	metal d orbitals				β -diketonate orbitals			olefin 9b ₂ orbital
	6b ₁	14a ₁	5a ₂	13a ₁	5b ₁ (π_3)	10b ₂ (n ₋)	12a ₁ (n ₊)	
tmhRh(C ₂ H ₄) ₂	7.50	—	7.9	—		8.9	(10.5)	10.01
acacRh(C ₂ H ₄) ₂	7.54	—	8.11	—	8.9	9.33	10.76	10.22
tfaRh(C ₂ H ₄) ₂	7.96	8.56	(8.7)	(8.8)	9.4	9.79	11.2	10.64
hfaRh(C ₂ H ₄) ₂	8.34	—	9.06	—	9.94	10.32	11.8	11.1
tmhRh(C ₃ H ₆) ₂	7.27	—	7.76	—		8.7	10.2	9.68
acacRh(C ₃ H ₆) ₂	7.43	—	7.92	—	(8.8)	9.13	10.5	9.85

^a Symmetry assignment and numbering are taken from the CNDO calculations on the [acacCo(CO)₂] and [acacCo(C₂H₄)₂] complexes.

^b Shoulders in the spectra are indicated by parentheses.

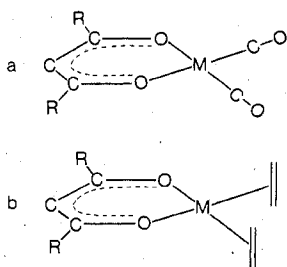


Figure 1. Structures of (β -diketonato)M(CO)₂ (a) and (β -diketonato)M(olefin)₂ (b).

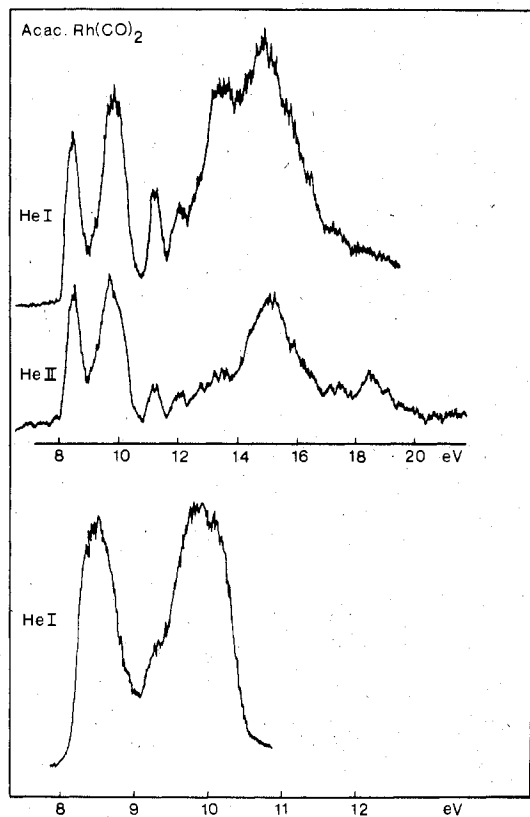


Figure 2. He I and He II spectra of acacRh(CO)₂ together with an expanded He I spectrum of the first bands.

ments given below. On the basis of these calculations, approximate orbital representations have been made which are represented throughout the text.

The spectra show a very crowded, low-energy region (7–12 eV) with many more or less well-resolved bands. The 12–

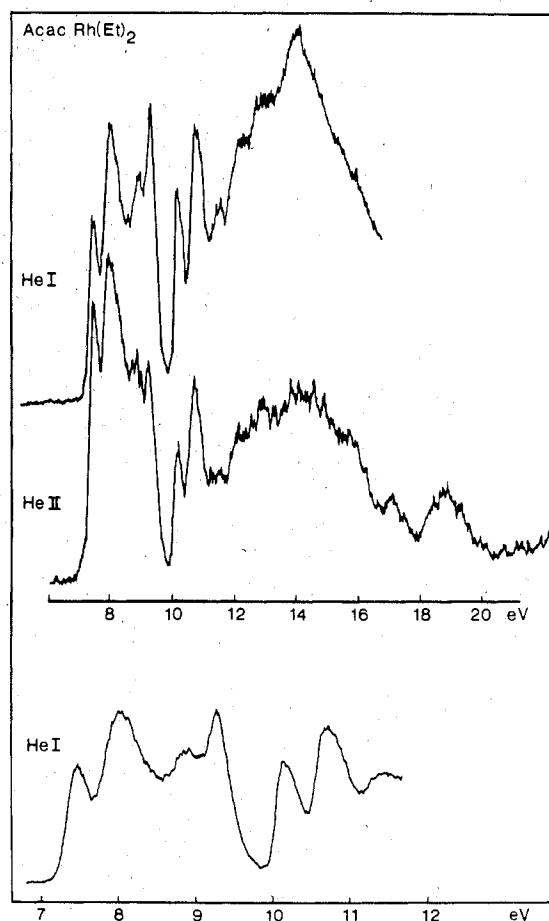


Figure 3. He I and He II spectra of acacRh(C₂H₄)₂ together with an expanded He I spectrum of the first bands.

20-eV region shows a broad band with some structure. This band contains, as is known from many investigations of organometallic complexes, most of the ligand σ orbitals. Because of crowding of this region detailed assignments are virtually impossible.

The low-energy region should belong to electrons ionizing from (a) olefin orbitals, (b) β -diketone orbitals, and (c) metal d orbitals. In the following sections assignments are given for the above-mentioned orbitals in the various complexes. Relevant spectra are shown in Figures 2–7, and the observed vertical ionizations are collected in Tables I and II.

The Rhodium Complexes. We will discuss the acac complexes in considerable detail. The assignment for the com-

Table II. Vertical Ionization Energies of (β -diketonate)IrL₂ (L = CO, C₂H₄, C₃H₆) Complexes^{a,b}

	metal d orbitals				β -diketonate orbitals		
	14a ₁	5b ₂	13a ₁	4a ₂	4b ₁ (π_3)	11b ₂ (n ₋)	12a ₁ (n ₊)
tmhIr(CO) ₂	8.2	8.48	9.1	9.6	9.9		(11.3)
acacIr(CO) ₂	8.42	8.69	9.2	9.9	9.9	10.3	11.6
tfaIr(CO) ₂	8.75	9.17	9.7	10.4		11.0	12.3
hfaIr(CO) ₂	9.14	9.26	10.17	(10.9)	10.9	11.4	12.7

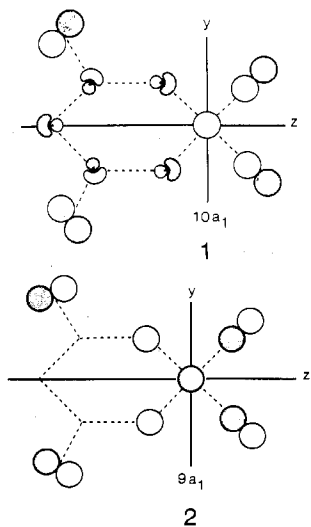
	metal d orbitals				β -diketonate orbitals			olefin 9b ₂ orbital
	6b ₁	14a ₁	5a ₂	13a ₁	5b ₁ (π_3)	10b ₂ (n ₋)	12a ₁ (n ₊)	
tmhIr(C ₂ H ₄) ₂	7.32	7.8	8.2	8.8	9.12		c	(10.3)
acacIr(C ₂ H ₄) ₂	7.36	7.83	8.37	8.86	9.35	(9.5)	11.2	10.41
tfaIr(C ₂ H ₄) ₂	7.70	8.17	8.80	9.25	9.79	10.05	11.5	10.90
acacIr(C ₃ H ₆) ₂	7.15	7.60	8.15	8.59	9.05	(9.3)	10.6	10.01
tfaIr(C ₃ H ₆) ₂	7.57	7.99	8.61	8.99	9.54	9.7	11.0	10.36

^a Symmetry assignment and numbering are taken from the CNDO calculations on the [acacCo(CO)₂] and [acacCo(C₂H₄)₂] complexes. ^b Shoulders in the spectra are indicated by parentheses. ^c Not observed due to severe crowding of orbitals.

plexes with the other β -diketonates proceeds approximately via the same reasonings.

a. The Olefin Orbitals. Comparing the PE spectra of [acacRh(CO)₂] with the spectra of [acacRh(C₂H₄)₂] in the 10–14-eV region reveals an extra band in the latter spectrum at 10.22 eV. This band should be assigned to ionizations from the π (C=C) orbitals of the ethylene ligands, since for the free ligand this orbital is found at 10.51 eV.¹⁵ Comparing the spectrum of [acacRh(CO)₂] with that of [acacRh(C₃H₆)₂] also indicates an extra band, now lying at 9.85 eV (9.82 eV in the free propylene ligand¹⁵). The destabilization of this band on going from ethylene to propylene due to the electron-donating effect of the methyl group gives more evidence for assignment of this band to olefin ionizations.

In these complexes which all have C_{2v} symmetry the two olefin orbitals should transform as a₁ and b₂, which interact differently with different metal orbitals. According to the CNDO calculations the a₁ combination mixes into two low-lying, very delocalized orbitals giving rise to 9a₁ and 10a₁ (1 and 2). These orbitals have substantial electron density on the acac ligand together with some density in the metal s orbital.



(15) Turner, D. W.; Baker, C.; Baker, A. D.; Brundle, C. B. "Molecular Photoelectron Spectroscopy"; Wiley-Interscience: New York, 1970.

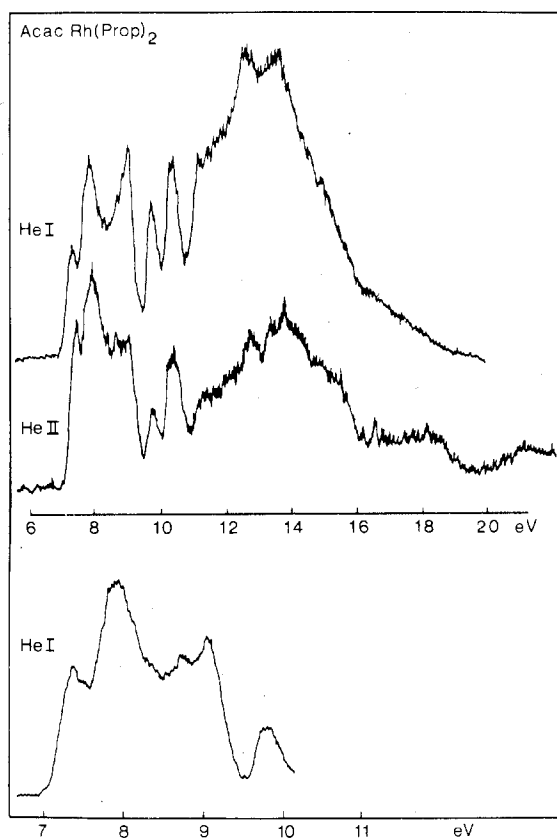


Figure 4. He I and He II spectra of acacRh(C₃H₆)₂ together with an expanded He I spectrum of the first bands.

The b₂ combination remains much more localized and provides σ donation from the olefins into the empty d_{yz} orbital of the metal, yielding the 9b₂ orbital. This 9b₂ orbital is calculated at 15.13 eV in the cobalt complex, while the 9a₁ and 10a₁ orbitals are approximately 3 eV more stable. The ~5-eV difference between the cobalt calculation and the olefin IE in [acacRh(C₂H₄)₂] is not unexpected since in an earlier study^{2b} of Fe(CO)₄ olefin complexes using this CNDO scheme the π (C=C) orbital in Fe(CO)₄C₂H₄ was calculated at 15.25 eV (10.56 eV experimentally³), and we do not expect large differences between Co and Rh. A correction of approximately 5 eV for these orbital eigenvalues has to be applied for an agreement with experiment.

So we assign the 10.22-eV band in [acacRh(C₂H₄)₂] to the 9b₂ orbital. The 9a₁ and 10a₁ orbitals are likely to be merged in the broad band in the 12–16-eV region.

b. β -Diketone and Metal Ionizations. Olefin Complexes. First we shall discuss [acacRh(C₂H₄)₂] in relation with the results from UPS measurements on the free acac ligand. Acac exists in the vapor phase predominantly in the enol form.^{6,13} In the low-energy region two ionizations have been observed, first at 9.07 eV the π_3 ionization and then at 9.60 eV the n₋ combination of the oxygen lone pairs.⁶ In the high-energy region the remaining π orbitals, the n₊ oxygen lone-pair combination, and the other σ ionizations are present. There is still some doubt concerning the precise assignment of the π_2 and n₊ orbitals,⁶ but, according to CNDO/S calculations,¹² they are in the broad band centered at approximately 12 eV.

In the other β -diketonates the π_3 and n₋ orbitals are readily assigned in the low-energy region.⁶ The only difficulty arises in tmh where the π_3 and n₋ orbitals are very close together, but as we shall see, this is of some help in the assignment of the complexes.

When we look at the spectrum of $[\text{acacRh}(\text{C}_2\text{H}_4)_2]$, we still have to account for four bands in the 8–10-eV region. In this region the acac π_3 and n_- ionizations are expected together with ionizations from the metal d orbitals. On the basis of relative intensities the bands at 8.94 and 9.33 eV resemble the bands in the free ligand,⁶ but this is not a very strong argument, since in most acac complexes the bands are less resolved. Some further evidence for the assignment of the π_3 and n_- orbitals can be found by comparison of the He I spectrum of $[\text{acacRh}(\text{C}_2\text{H}_4)_2]$ with that of $[\text{tmhRh}(\text{C}_2\text{H}_4)_2]$. The splitting between the two bands of 8.94 and 9.33 eV in $[\text{acacRh}(\text{C}_2\text{H}_4)_2]$ resembles the splitting in the free ligand, while in $[\text{tmhRh}(\text{C}_2\text{H}_4)_2]$ the band at 8.93 eV shows, just as in the free tmh ligand, two (nearly) degenerate ionizations.

On the basis of this, the bands at 8.94 and 9.33 eV in $[\text{acacRh}(\text{C}_2\text{H}_4)_2]$ are assigned to ionizations from the π_3 and n_- orbitals ($5b_1$ and $10b_2$, according to the calculations).

In the low-energy region of the ethylene and propylene complexes, two more bands have to be assigned which appear in a 1:3 intensity ratio at 7.54 and 8.11 eV (ethylene) and 7.43 and 7.92 eV (propylene), respectively. Since we have already assigned the acac and the olefin orbitals, we have to assign these bands to ionizations from the four metal d orbitals. Another argument for this assignment is found in the intensity increase of these bands on going from He I to He II radiation. This is a common phenomenon for metal d orbitals and is a well-established assignment criterion for transition metals of the first row, although there are some exceptions. Since there are not enough experimental data in the literature concerning the cross-section behavior of 4d and 5d orbitals, the intensity increase alone cannot be used as an unambiguous assignment criterion. But, since the metal d orbitals in $[\text{acacRh}(\text{C}_2\text{H}_4)_2]$ and $[\text{acacRh}(\text{C}_3\text{H}_6)_2]$ have already been assigned by other means, it is now clear that the cross-section variation can be used as an assignment criterion in this class of complexes.

The assignments given above are confirmed by the CNDO calculations on the cobalt model complex. According to these calculations the four highest occupied MO's ($6b_1$, $14a_1$, $5a_2$, $13a_1$) are essentially metal d in character. The fifth and sixth MO's ($5b_1$ and $10b_2$) are mainly localized on the acac ligand (π_3 and n_- , respectively).

The ordering of the metal d orbitals is not easily determined. No experimentally based assignment criteria are available to give unambiguous assignments, and since results from sophisticated MO methods are not available, nothing definite can be said. However, the agreement of the CNDO results with experiment is much better than could be expected. In the calculation, approximately the same spacing between the orbitals is calculated as is found in the experiment. The 1:3 intensity ratio found in the spectra can thus be explained, and the tentative assignments given in Table I are thus based on the calculated results.

The Carbonyl Complexes. For the $[\text{acacRh}(\text{CO})_2]$ complex only two bands are observed in the low-energy region (8–10 eV). He I/He II intensity differences indicate that the metal d orbitals are present in both bands. In the He II spectrum the first band and the low-energy side of the second band increase in intensity which indicates that the metal d orbitals have to be assigned to those bands. The shoulder on the high-energy side of the second band should accordingly be assigned to ionizations from the π_3 and n_- acac orbitals. It is obvious that in the CO complex the four d orbitals are split into two accidentally (nearly) degenerate sets each of two orbitals.

The CNDO calculations also show this splitting pattern of the metal d orbitals, first the $14a_1$ and $5b_1$ orbitals and then, about 1 eV more stable, the almost degenerate $13a_1$ and $4a_2$ orbitals. The next two MO's are again predominately the π_3

($9a_1$) and n_- ($11b_2$) orbitals. So the calculated spitting pattern of the metal d orbitals and the relative ordering of the MO's are again in agreement with the experiment.

With the first bands in $[\text{acacRh}(\text{CO})_2]$ being assigned, the other bands must originate from the acac and the CO ligands.

The CO 5σ , 4σ , and 2π orbitals are in the 14–20-eV region as is known from comparison with free CO¹⁵ and with, for instance, $\text{Fe}(\text{CO})_5$.^{2a} The bands in the 10–14-eV region are then to be assigned to ionizations from the acac ligand. There is a well-resolved band visible at 11.22 eV. This band is observed in the spectra of all acac complexes at slightly different positions. This band can either be due to ionizations from the π_2 orbital or from the n_+ oxygen lone-pair combination, which are probably nearly degenerate in the free ligand as was mentioned before. A destabilization of about 0.8 eV is however not expected for π_2 since this orbital will not strongly be stabilized since the π_2 orbital is not very different from the π_3 orbital, which is hardly affected upon coordination. Therefore, assignment of the 11.22-eV band to π_2 is not likely. Some further support for the assignment of this band to n_+ comes from the He I/He II intensity variation of this band in the olefin complexes. In all complexes this band does not decrease in intensity as much as the other ligand bands. This might also indicate that this band originates from the n_+ lone-pair oxygen ionizations which are known to have a higher cross section in He II than in He I. But this is not conclusive evidence since there are many ionizations in this region and coordination to the metal could change the cross-section behavior of this MO. The reason for the destabilization of the n_+ orbital is discussed in a subsequent section.

According to the CNDO calculations four ionizations should be present in the 11–14-eV region in $[\text{acacRh}(\text{CO})_2]$. The highest occupied one in this region is the n_+ orbital ($12a_1$), which is in agreement with the assignment given above. The remaining three ionizations ($11a_1$, $3a_2$, and $10b_2$) can then be assigned tentatively to the two bands at 11.8 eV ($11a_1$) and ~13 eV ($3a_2$ and $10b_2$).

The Iridium Complexes. At first glance the spectra of the iridium complexes are rather more complicated than the spectra of the rhodium analogues. The major differences however are only in the low-energy region (7–10 eV).

The assignment of the olefin π and β -diketone π_3 and n_- orbitals proceeds via the same reasoning as for the rhodium complexes. The assignment of the n_+ orbital is more difficult due to the overlapping of some acac and olefin bands in this region. The tentative assignment which is given in Table II is based on the spectra of the carbon monoxide complexes and on the shifts which have been found in the analogous rhodium complexes.

The metal d orbitals are again assigned by comparison of the spectra. He I/He II cross-section differences confirm the assignments. The iridium 5d orbitals are much more split than the rhodium 4d ones. In most spectra of the olefin complexes, four separate bands are seen, which is expected since Ir(I) has a d^8 electron configuration. The carbon monoxide complexes show less bands, but here overlapping occurs with the β -diketone orbitals as is clearly seen in the He II spectra.

Detailed assignments of the metal ionizations are again very difficult, owing to the lack of experimentally based assignments criteria. The overall trends in the IE's are however the same in the iridium complexes as in the rhodium complexes. So it is assumed that the ordering of the metal orbitals is the same as in the rhodium complexes and as in the cobalt model complexes.

Discussion

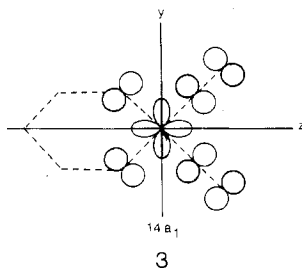
Assignment Criteria. The assignment criteria used have provided information concerning the unambiguous assignment

of most of the orbitals in the low-energy region. Emphasis was placed on empirical correlations with related complexes and on He I/He II intensity differences.

The assignment of the metal d orbitals is more ambiguous. The extended CNDO calculations on the cobalt model complexes¹² give results which are in good agreement with the spectra of the rhodium complexes, but this can be fortuitous. Still the question of the detailed assignment is somewhat academic since the ordering of the orbitals in a PE spectrum need not be the ordering in the ground state. Differential relaxation owing to different percentages of metal d character in the various orbitals can cause reversal of the metal d levels.¹⁶ This possible deviation of Koopmans' theorem is not the only factor which can obstruct an unambiguous assignment. Other factors are, for instance, the relativistic effects such as spin-orbit coupling, which are known to play an important role in transition metals of the second and third rows. These effects will be larger for iridium than for rhodium, and this could be one of the causes for the greater splitting in the metal-d spectra of the iridium complexes.

The calculations however give an approximate description of the bonding interactions in the model complexes, and the good overall agreement with the experimental results of the rhodium complexes may give confidence in the transferability of the theoretical results from cobalt to rhodium and iridium.

Bonding Interactions in the Various Complexes. Theoretical Bonding Model. The Carbonyl Complexes. Bonding between the metal and the carbonyl ligand occurs, according to the calculations, predominantly via π back-donation from occupied metal orbitals to the empty π^* orbitals of the CO ligands.¹⁷ In the complexes under study here there are, according to the calculations, three metal orbitals suitable for π back-bonding. First is the $14a_1$ orbital (a combination of d_{z^2} and $d_{x^2-y^2}$ orbitals), which is capable of in plane π back-bonding (3). The



(16) Guest, N. F.; Higginson, B. R.; Hillier, I. H.; Lloyd, D. R. *J. Chem. Soc., Faraday Trans. 2* **1975**, 902.

(17) There is still considerable controversy in the literature concerning the importance of π back-bonding in the metal-CO bond. Hartree-Fock and DV $X\alpha$ calculations indicate significant π back-bonding for the transition-metal carbonyls while MS $X\alpha$ calculations stress the importance of σ donation and the insignificance of π interactions.¹⁸ We of course do not rule out the possibility of σ donation, but in our opinion data from vibrational spectroscopy indicate the importance of π back-bonding. The presence of the M-CO σ bond does not have a large influence on the C=O bond. In contrast, the presence of π bonding should cause a considerable decrease in the $\nu(\text{C=O})$ since π bonding affects the C=O bond. In pure σ complexes such as $\text{H}_3\text{B}\cdot\text{CO}$ ¹⁹ $\nu(\text{C=O})$ is raised with respect to the free CO ligand (2143–2164 cm^{-1}) (compare also the value of $\nu(\text{C=O})$ for CO adsorbed on ZnO at 2210 cm^{-1}).²⁰ In transition-metal carbonyl complexes, the $\nu(\text{C=O})$ stretching frequencies are lower than 2143 cm^{-1} . In the complexes under study here, the CO stretching frequencies are found at 2082 and 2011 cm^{-1} ($\text{acacRh}(\text{CO})_2$) and at 2073 and 1999 cm^{-1} ($\text{acacIr}(\text{CO})_2$). We must therefore conclude that π back-bonding plays an important role in these dicarbonyl complexes.

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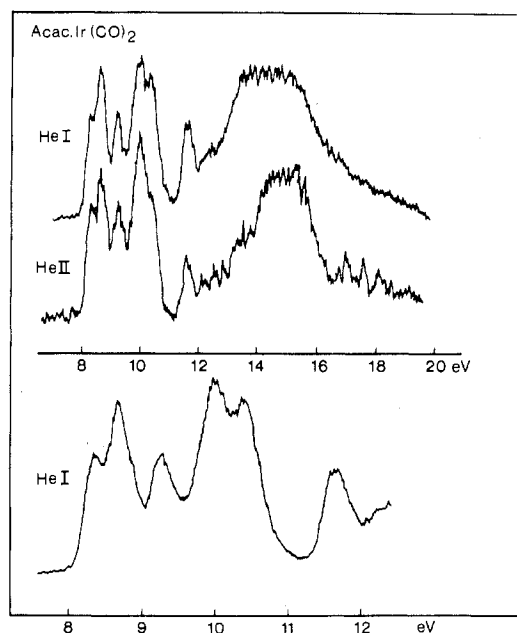
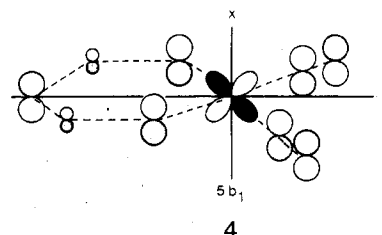
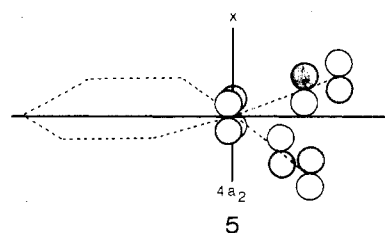


Figure 5. He I and He II spectra of $\text{acacIr}(\text{CO})_2$ together with an expanded He I spectrum of the first bands.

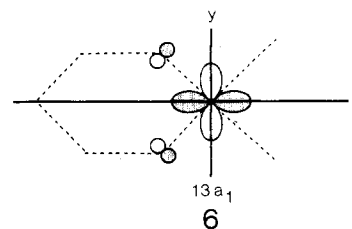
second orbital ($5b_1$) provides π back-bonding from the d_{xz} orbital to the π^*_x CO orbital (4). Third, the d_{xy} orbital ($4a_1$),



which is predominantly metal lone pair in character, also has a small capability for π bonding with the π^*_x CO orbitals (5).



The fourth occupied metal orbital ($13a_1$) is also predominantly lone pair in character but is also σ antibonding with respect to the $\text{acac } n_+$ orbital (6).



Metal-carbonyl bonding also occurs via σ donation of electrons from occupied CO 5σ orbitals to the empty metal d_{yz} orbital ($8b_2$ and $9b_2$ in the complex).

Metal-acac interactions can in principle also occur via σ bonding and π back-bonding. The calculations however in-

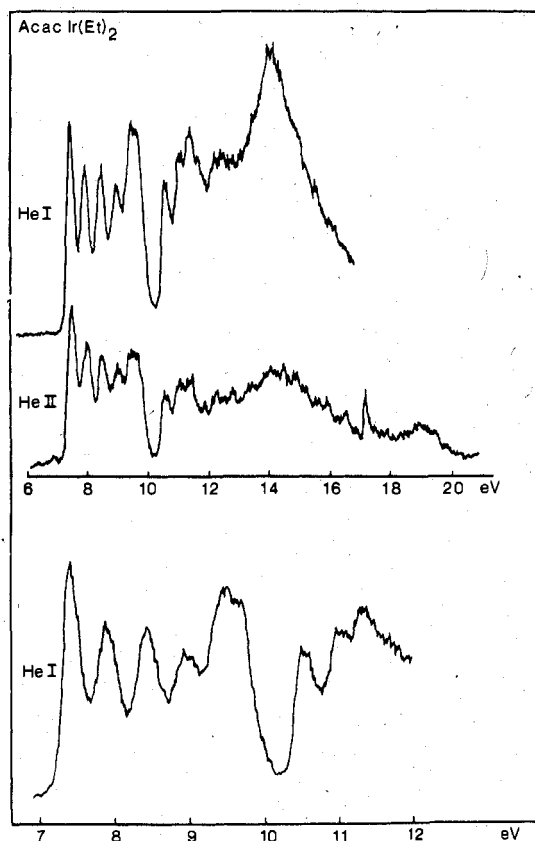


Figure 6. He I and He II spectra of $\text{acacIr}(\text{C}_2\text{H}_5)_2$ together with an expanded He I spectrum of the first bands.

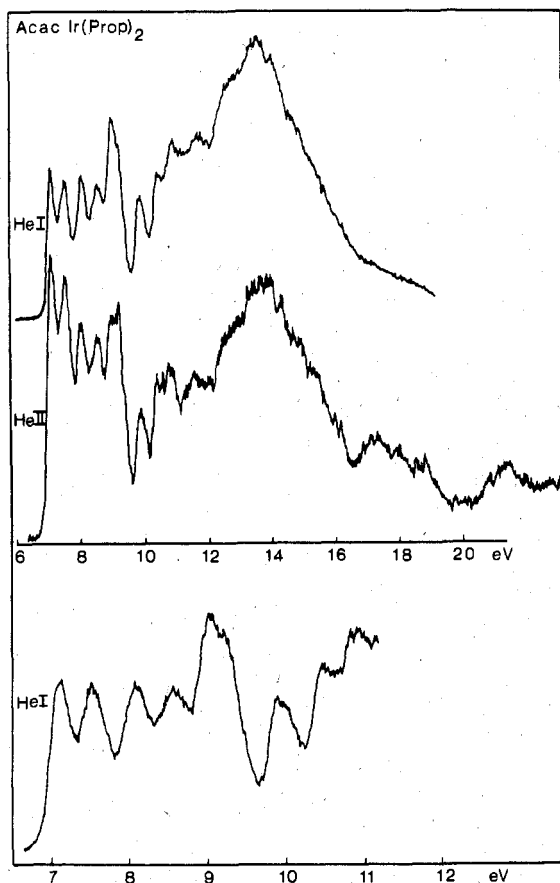


Figure 7. He I and He II spectra of $\text{acacIr}(\text{C}_3\text{H}_7)_2$ together with an expanded He I spectrum of the first bands.

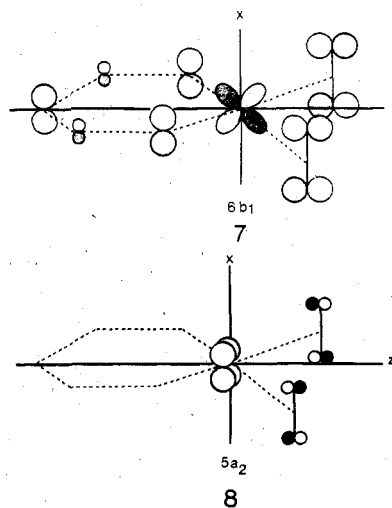
dicates that there is no empty π^* orbital on the acac ligand interacting with an occupied metal orbital. This absence of π back-bonding is also confirmed by a PE study on $\text{Co}(\text{acac})_3$ and related complexes by Brittain et al.²¹ σ bonding can only occur via donation from the n orbital to the empty d_{yz} orbital ($11b_2$ in the complex).

Bonding in the free ligand with hydrogen is of course very different. OHO bonding occurs via the n oxygen lone-pair combination, while the n orbital is nonbonding with respect to hydrogen. This causes the decrease in $n+n$ splitting upon coordination.

The Olefin Complexes. In the bis olefin complexes the in-phase and out-of-phase combination of the $\pi(\text{C}=\text{C})$ MO's generate new symmetry orbitals, which transform as a_1 and b_2 in C_{2v} symmetry. The accidental degeneracy of these orbitals will not be removed unless they are involved in some metal-ligand and/or interligand interaction.

The b_2 orbital combines with the empty d_{yz} orbital and provides the normal σ donation as is described by the Chatt-Dewar-Duncanson (CDD) model.^{22,23} The a_1 orbital combines with orbitals of the metal-acac moiety as was described in an earlier section (1 and 2).

π back-bonding occurs via donation from the d_{xz} and d_{xy} orbitals to π^* levels of the olefins ($6b_1$ and $5a_2$, respectively), just as in the carbonyl complexes 7 and 8.



The character of the a_1 metal orbitals changes significantly on going from the bis carbonyl to the bis olefin complexes, as is seen in the orbital diagrams 9 and 10. This presents simple correlations and interpretations of the trends in the metal orbitals.

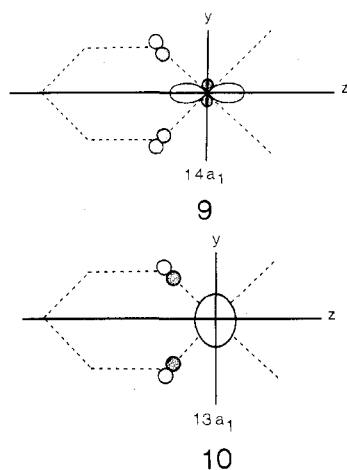
Correlation of the Spectral Data with Bonding Interactions. The interpretation of IE differences between the complexed and free ligands in terms of charge shifts and bonding interactions is of course only justified when Koopmans' theorem is valid or when deviations are the same in both cases. The validity of this cannot be determined but, as we have seen in an earlier study concerning iron tetracarbonyl olefin complexes,^{2b} severe deviations are not expected.

The Olefin Ionizations. Interligand interaction can, as was mentioned above, prevent interpretation of the olefin b_2 IE's in terms of bonding interactions and charge shifts. However, in these complexes, interligand interactions will be small, owing to the relatively large ethylene-ethylene separation. That it is of minor importance is clearly seen when we compare the

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ethylene complexes with the propylene complexes. If the destabilization of the b_2 orbital with respect to the free ligand in $[\text{acacRh}(\text{C}_2\text{H}_4)_2]$ is caused by interligand interaction, the same effect, perhaps even larger due to the more bulky propylene ligands, should be seen in $[\text{acacRh}(\text{C}_3\text{H}_6)_2]$. However, no destabilization is seen on comparing the IE of the free propylene with the IE of the complexed ligand. Thus the stabilizations and destabilization of the olefin levels upon complexation can, in first order, be interpreted as resulting only from σ and π metal-ligand interactions. Based on elementary MO calculations, it is possible to rationalize the shift in the $9b_2$ orbital with respect to the IE of free ethylene. Bonding occurs, as was mentioned before, via three interactions. First, there is σ donation from the a_1 olefin combination to the metal and the β -diketonate. This yields a decrease in electron density on the olefinic ligands and thus causes a stabilization of the MO's mainly localized on these ligands. Second, there is σ donation from the b_2 combination to the empty d_{yx} orbital. This also causes a stabilization of the $9b_2$ orbital. Third, there is π back-donation from the metal to π^* orbitals on the olefin. This should cause an increase in electron density on the olefins and thus a destabilization of the orbitals.

The observed destabilization of the $9b_2$ orbital with respect to the IE of the free ligand (10.51 eV^{15}) can only lead to the conclusion that the π -back-bonding interaction is very important in $[\text{acacRh}(\text{C}_2\text{H}_4)]$.

Variation of the substituents on the β -diketonate ligand has a large influence on the IE of the b_2 olefin orbital. In the tfa and hfa complexes a stabilization of this orbital is seen with respect to the acac complex, while in the tmh complex a destabilization occurs. In the rhodium bis ethylene complexes, this IE varies from 10.01 (tmh) to 11.07 eV (hfa). This large change in IE must be caused by an increase in σ bonding and/or a decrease in π back-bonding.²⁴ The shifts are governed by the normal inductive effects of the substituents.

The CNDO calculations suggest that this very large substituent dependence is caused by the $9a_1$ and $10a_1$ orbitals, which have significant electron density both at the β -diketonate moiety and at the olefins.

The shifts of the olefin orbital energies in the propylene complexes, when compared again with those of the free ligand, show a somewhat different behavior. In $[\text{acacRh}(\text{C}_3\text{H}_6)_2]$ no destabilization is seen (the olefin IE (9.85 eV) is comparable with the IE of the free ligand (9.72 eV adiabatic, 9.82 eV vertical¹⁵), which means that there is a decrease in π back-bonding or an increase in σ donation with respect to ethylene.²⁴ The general trend upon variation of the diketone is identical with the trends in the ethylene complexes. Owing to the limited number of propylene complexes measured a full com-

parison is not possible, but the shifts of the orbitals are very regular, so that it might even be possible to predict the values for the missing complexes, which either could not be measured owing to low volatility or could not be synthesized.

Going from Rh to Ir, a very consistent pattern is observed. The b_2 olefin orbital is always stabilized by 0.2–0.3 eV. According to the results of other spectroscopic techniques, the π -back-bonding capacity of Ir is only slightly larger than that of Rh. For instance the CO stretching frequencies in the rhodium and iridium carbon monoxide complexes differ only by 11 cm^{-1} . This minor increase in π -back-bonding capacity should cause a destabilization of the olefin orbitals. However a stabilization is found,²⁵ indicating that the increase in π back-bonding is accompanied by a larger increase in metal-olefin σ bonding. This higher σ -bonding capacity of iridium when compared with that rhodium is also observed in the PE spectra of $\text{HRh}(\text{PF}_3)_4$ and $\text{HIr}(\text{PF}_3)_4$ for the M–P σ bond.²⁶

Jesse et al.⁵ have published IR, ^{13}C NMR, ^1H NMR, and thermochemical data of these complexes. The agreement between their results and ours is quite satisfactory.

The β -Diketonate Ionizations. Shifts among the various β -diketonates are controlled by the normal inductive effects of the substituents. The fluoro-substituted β -diketonates have PE spectra in the low-energy region similar to those of acac itself,⁶ except for a similar increase in ionization potential of the bonds as a consequence of the strong $-I$ effect of fluorine. The PE spectrum of tmh shows a destabilization of the bands with respect to acac owing to the electron-donating capacity of the methyl groups.

In the spectra of the complexes under study, the n_- and n_+ ionizations are the most well-defined bands. The π_3 band is mostly hidden under the other bands or is only just visible as a shoulder on the other bands. Only the acac complexes will be discussed since the other series either are incomplete or show analogous trends.

The trends in the metal complexes are the same as the trends in the free β -diketonates. The π_3 and n_- bands are slightly shifted to lower energy, when compared with those of the free ligands. The carbonyl complexes show a stabilization of the π_3 and n_- ionizations, owing to the very strong electron-withdrawing character of the carbon monoxide ligands. As we have indicated in an earlier section, the n_+n_- splitting will be different in the complexes from the splitting in the free ligands, but nevertheless in the complexes the same trend is followed.

On going from Rh to Ir, the same trends are visible. There is however a uniform shift to higher ionization potential, and this can indicate, as we have mentioned before, a higher σ -bonding capacity of Ir when compared to Rh.

The Metal d Orbitals. The shifts in the metal d orbitals are very regular as was already shown in an earlier section.

The large destabilization on going from the carbonyl to the olefin complexes provides evidence for the larger π -back-bonding and/or the smaller σ -donating capability of the carbon monoxide ligands.

The shift to lower energy on going from ethylene to propylene and from hfa via tfa and acac to tmh is governed by the normal inductive effects of the substituents.

Conclusions

In general unambiguous assignments are possible by use of a number of assignment criteria. Consistent information concerning the ordering and the character of most of the bands in the low-energy region is obtained. There are observed, first,

(25) It could be argued that a decrease of interligand interaction, owing to the larger bond distances in the Ir complexes, is causing this effect. However, as we have indicated, interligand interaction is not likely to be of great importance in these complexes.

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(24) These effects of course can not be separated.

ionization from the metal d levels, second, ionizations from the β -diketonate ligand, and then, ionization from an olefin orbital.

The differences in electronic structure in these complexes are very well demonstrated in the shifts of the various orbitals. These shifts show that, when a substituent is introduced in a ligand, the electronic effect of this substituent affects the whole molecule. CNDO calculations on model complexes suggest that this is caused by low-lying orbitals which are delocalized over the entire molecule. The trends in the IE's follow the normal electron-withdrawing and -donating properties of the substituents. Shifts in the olefin orbitals can be interpreted in the Chatt-Dewar-Ducanson model as differences in σ and

π interactions. π back-bonding especially is of importance in the metal-olefin bond.

The stabilization of the ligand orbitals on going from rhodium to iridium can indicate that σ bonding becomes more important in the iridium complexes.

Registry No. tmhRh(CO)₂, 24151-60-8; acacRh(CO)₂, 14874-82-9; tfaRh(CO)₂, 18517-13-0; tmhRh(C₂H₄)₂, 64466-15-5; acacRh(C₂H₄)₂, 12082-47-2; tfaRh(C₂H₄)₂, 69372-77-6; hfaRh(C₂H₄)₂, 55188-59-5; tmhRh(C₃H₆)₂, 69372-72-1; acacRh(C₃H₆)₂, 12282-38-1; tmhIr(CO)₂, 74684-28-9; acacIr(CO)₂, 14023-80-4; tfaIr(CO)₂, 14024-04-5; hfaIr(CO)₂, 14049-69-5; tmhIr(C₂H₄)₂, 74684-29-0; acacIr(C₂H₄)₂, 52654-27-0; tfaIr(C₂H₄)₂, 74684-30-3; acacIr(C₃H₆)₂, 66467-05-8; tfaIr(C₃H₆)₂, 74684-31-4.

Contribution from the Anorganisch Chemisch Laboratorium, University of Amsterdam, J. H. van't Hoff Instituut, 1018 WV Amsterdam, The Netherlands, and the Departments of Chemistry, The University, Southampton S09 5NH, United Kingdom, and Tulane University, New Orleans, Louisiana 70118

Photochemistry of Piperidine Pentacarbonyl Complexes of the Group 6B Metals Isolated in an Argon Matrix at 10 K

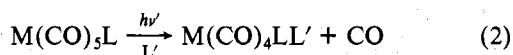
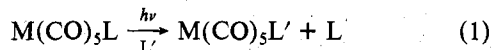
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Received March 26, 1980

Short-wavelength photolysis ($\lambda = 229, 254$ nm) of $M(\text{CO})_5(\text{pip})$ complexes (pip = piperidine; $M = \text{Cr, Mo, W}$) in Ar matrices at 10 K resulted in the formation of $M(\text{CO})_4\text{L}$ species with C_s symmetry; long-wavelength photolysis ($\lambda = 366, 405$ nm) caused M-L bond breaking and formation of $M(\text{CO})_5$. The structures of the photoproducts were determined by ¹³CO labeling and force field calculations. The piperidine complexes showed a metal-dependent photochemistry and a reduced photochemical efficiency with respect to other $M(\text{CO})_5\text{L}$ complexes at all wavelengths. The results are compared with studies of $M(\text{CO})_5\text{L}$ complexes ($M = \text{Cr, W}$; $L = \text{pyridine, pyrazine, NMe}_3$), both in matrices at 10 K and in solutions at room temperature, and are explained by d-orbital energy diagrams derived from photoelectron spectra.

Introduction

The solution photochemistry of $M(\text{CO})_5\text{L}$ complexes ($M = \text{Cr, Mo, W}$; $L = \text{amine, imine, phosphine}$) has been extensively studied by several authors.¹⁻¹⁰ These studies demonstrated that the photochemistry of these complexes is dependent on the wavelength of irradiation, the ligand L , and the metal. Two photochemical reactions are possible: eq 1 and 2. The quantum yields of both reactions are dependent



on the wavelength; e.g., reaction 1 is dominant at long wavelengths, whereas reaction 2 becomes increasingly important at shorter wavelengths. Zink reported that nitrogen-donor complexes show efficient ligand photosubstitution, with a reduced quantum yield for reaction 2, that phosphorus-donor complexes undergo both reactions with high quantum yields, and that a third class of ligands, e.g., CS, showed low quantum yields for both reactions.⁵ These conclusions were based on photolysis with only two wavelengths, namely, 405 and 436 nm. The metal dependence of both photochemical reactions has been demonstrated in a study by Darensbourg et al.⁷ An increased quantum yield of CO substitution was found on going from W and Mo to Cr. In the presence of ¹³CO, exclusively equatorial carbonyl photosubstitution oc-

curred, leading to the suggestion that a C_s intermediate is involved in these photochemical reactions.⁷

In order to prove the structure of the intermediates involved in the photochemical reactions of substituted group 6B hexacarbonyls, we carried out matrix isolation studies.¹¹⁻¹⁸ Rest proved that bulky ligands can be generated in matrices and found evidence for the formation of $W(\text{CO})_5$ after photolysis

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