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(43) Dr. Joe Norman, Jr. (private communication), has suggested that the sensitivity of the minimum-energy-cluster electronic configuration to spin-polarization effects (vis-ã-vis Rh_2 SCF–Xα–SW calculations[27]) could favor the nearby $2\sigma_g{}^1 1\pi_g{}^2 1\sigma_u{}^1$ state over our preliminary Xα spin-restricted $2\sigma_g{}^2 1\pi_g{}^2 1\sigma_u{}^0$ ground state. Moreover, qualitative oscillator strength arguments (based on Cu_2,Ag_2 computations[33a]) imply that a *blue shift* of the entire calculated optical spectrum by about 7000 cm^{-1} (corresponding to shorter Co–Co and Rh–Rh distances of 2.0 and 2.2 Å, respectively; cf. the 2.32- and 2.39-Å metal–metal bond lengths employed in the existing SCF–Xα–SW calculations) would necessitate a reassignment of the most prominent bands of Co_2 and Rh_2 (270–350 nm) to $2\sigma_g \rightarrow 2\pi_u$ and $1,2\sigma_g \rightarrow 1,2\sigma_u$ excitations. In this case, cluster-support interactions may not be quite as pronounced as our discussion of the data presented in Table VI leads one to believe (see the last section of this paper).
(44) Although a one-electron transition for Rh_2 at 344 nm will only reduce the formal bond order from 2 to 1 (according to the assignments of Table V and Figure 9), excitation at 344 nm provides more than enough energy to photodissociate the Rh–Rh bond, especially in a rare gas matrix environment. (The bond dissociation energy of the Rh_2 molecule has been estimated from high-temperature Knudsen cell effusion-mass spectrometric data to be 67 kcal/mol: D. L. Cocke and G. A. Gingerich, *J. Chem. Phys.* **60**, 1958 (1974).) One must also be alert to the fact that the uncertainty in determining the extent of orbital contributions to the Rh–Rh bond from Xα methods may make it impractical to assign a formal bond order to Rh_2.

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An Electronic Spectroscopic Study of Bridge-Bonded Dirhodium Octacarbonyl

A. J. LEE HANLAN, GEOFFREY A. OZIN,* and HARRY B. GRAY

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The thermally induced (15–35 K) dimerization reaction of the 17-electron species $Rh(CO)_4$ (synthesized from Rh/CO $\simeq 1/10^4$; 15 K matrix cocondensations) to the bridge-bonded form of $Rh_2(CO)_8$, originally detected by matrix infrared spectroscopy, has now been monitored by electronic absorption spectroscopy. In this way the electronic spectrum of $Rh_2(CO)_8$ is defined and compared with corresponding spectroscopic data for the bridge-bonded form of $Co_2(CO)_8$. An intense band in the spectrum of $Rh_2(CO)_8$ at 260 nm is assigned to a $\sigma \rightarrow \sigma^*$ transition, whereas a strong MLCT absorption system is observed at about 225 nm. The $Rh_2(CO)_8$ $\sigma \rightarrow \sigma^*$ transition is blue-shifted from that found in $Co_2(CO)_8$ (282 nm), as expected.

Introduction

Considerable work has been undertaken to understand the electronic spectra of metal–metal-bonded $M_2(CO)_n$ and $M_2(CO)_nL_m$ complexes.[1] On the other hand, very little has appeared concerning binuclear metal carbonyl complexes that contain bridging carbonyl moieties. Recently Gray published[1b] an interpretation of the electronic spectra of $Co_2(CO)_8$ in both the nonbridged and CO-bridged isomeric forms. A $\sigma \rightarrow \sigma^*$ absorption system was identified in the spectrum of each isomer, although the assignment in the case of the bridge-bonded molecule was not as clear-cut as it was for nonbridged $Co_2(CO)_8$.

In an earlier publication we described[2] the synthesis and characterization of $Rh_2(CO)_8$ by Rh-atom cryochemical techniques in conjunction with matrix-isolation infrared spectroscopy. The dimer was identified by Rh concentration and matrix-annealing experiments and was found to exist exclusively in the bridge-bonded form.[3] We have now measured the electronic spectrum of $Rh_2(CO)_8$, and comparisons with data collected previously for $Rh(CO)_4$,[4] $Co(CO)_4$,[4] and bridge-bonded $Co_2(CO)_8$[1b] have allowed us to assign the two most intense ultraviolet features.

Experimental Section

Through use of Rh/CO $\simeq 1/10^4$ and 15 K deposition conditions, the electronic absorption spectra consist primarily of $Rh(CO)_4$ as seen through the eye of the corresponding infrared experiment,[2] recorded on the same sample. Temperature-programmed annealing experiments in the range 15–35 K induce decay of all of the absorptions associated with $Rh(CO)_4$, with accompanying growth of several new absorptions attributable to $Rh_2(CO)_8$.[2] Rhodium metal was supplied by A. D. MacKay, New York, and research grade $^{12}C^{16}O$ (99.999%) by Matheson of Canada. Rh/CO matrices were deposited on a NaCl optical window cooled to 15 K by an Air Products Displex closed-cycle helium refrigerator. Absorption spectra were recorded on a Varian Techtron 635 UV-visible spectrophotometer.

*To whom correspondence should be addressed at Lash Miller Chemical Laboratories.

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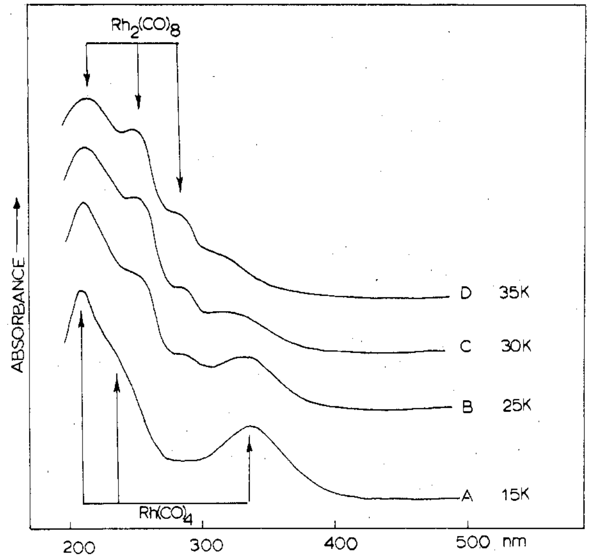

Figure 1. Ultraviolet spectra of rhodium atoms cocondensed with pure CO (Rh/CO ≃ 1/10⁴): (A) 15 K experiment showing spectroscopically isolated $Rh(CO)_4$; (B–D) warm-up experiments performed at 25, 30, and 35 K showing the gradual appearance of $Rh_2(CO)_8$ and concomitant decay of $Rh(CO)_4$ (with sequential IR/UV–vis monitoring from the same sample).

Table I. Electronic Absorption Band Positions (nm) for $M(CO)_4$ and Bridge-Bonded $M_2(CO)_8$ Molecules

$Co(CO)_4$[a]	$Co_2(CO)_8$[b]	$Rh(CO)_4$[a]	$Rh_2(CO)_8$	assignt
256 vs		210–215 vs	225 s	MLCT
269 m, sh		240 m, sh		MLCT
	282 s		260 s	$\sigma \rightarrow \sigma^*$
			290 m, sh[c]	
			320 m[c]	
315 m		335 m		LMCT
355 m				LMCT
346 m				LMCT

[a] Matrix-isolation study, ref 4. [b] Several other bands are observed; see ref 1b. [c] Not assigned. It is not even certain that the 320-nm feature is part of the $Rh_2(CO)_8$ spectrum, as it could represent a slight matrix concentration and temperature-dependent energy shift of the $Rh(CO)_4$ 335-nm band.

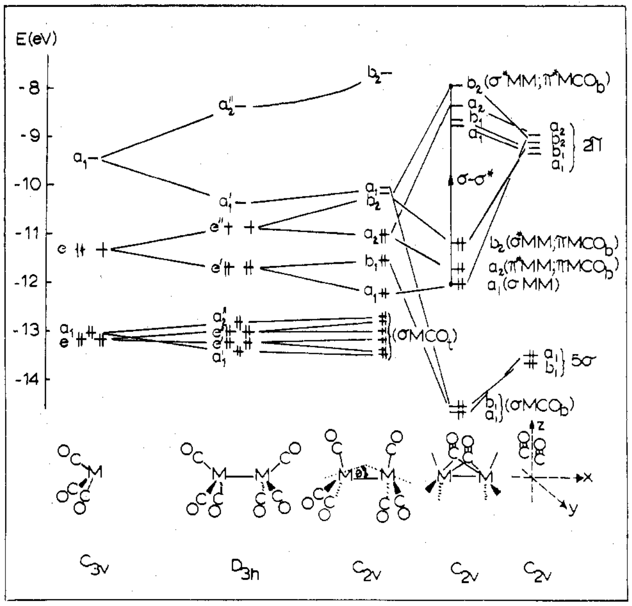

Figure 2. Fragment molecular orbital analysis of the bridge-bonded isomer of $Rh_2(CO)_8$ in C_{2v} symmetry based on Hoffmann and Thorn's[5b] original scheme for $Co_2(CO)_8$ and $Fe_2(CO)_8{}^{2-}$. (Main orbital contributions are indicated in this scheme.)

Results and Discussion

Figure 1 illustrates the electronic spectroscopic transformations observed for $Rh(CO)_4$ (the major product formed by using Rh/CO ≃ 1/10⁴; 15 K experimental conditions[2]) when a $Rh(CO)_4/CO$ matrix is gradually warmed. Above 30 K, the characteristic absorptions of $Rh(CO)_4$ begin to decay rapidly with the concomitant appearance of new bands attributable to the bridge-bonded dimer $Rh_2(CO)_8$. Under these conditions, according to our earlier infrared experiments, $Rh_2(CO)_8$ is the predominant species.[2] Band positions for $Rh_2(CO)_8$ are collected in Table I along with corresponding spectroscopic data for $Rh(CO)_4$,[4] bridge-bonded $Co_2(CO)_8$,[1b] and $Co(CO)_4$.[4]

We have chosen to adopt a fragment molecular orbital approach to facilitate assignment of the observed electronic spectrum of $Rh_2(CO)_8$. When Hoffmann's analysis[5] of $M_2(CO)_8$ molecules is followed, the orbitals comprising the M–M overlap region of the $M_2(CO)_6$ "sawhorse" residue (with $\theta = 58°$) are mainly d_{xz}, d_{yz}, σ, and π combinations (a_1, a_2, b_1, b_2), the d_{z^2}, d_{xy}, and $d_{x^2-y^2}$ orbitals having been incorporated earlier into the three low-lying M–CO_t σ bonds (a_1', e') of the two C_{3v} $M(CO)_3$ parent moieties comprising the C_{2v} $M_2(CO)_6$ fragment. Construction of the final orbital energy-level scheme for C_{2v} $M_2(CO)_8$ can then be achieved by combining the 5σ and 2π orbitals of two bridging carbonyls (with a C_{2v} disposition) with the C_{2v} $M_2(CO)_6$ fragment in the orientation shown in Figure 2. This carbonyl architecture generates a *pair* of low-lying M–CO_b σ bonds (a_1, b_1) bounded above by a group of *three* orbitals having considerable M–M σ- and π-bonding character (a_1, a_2, b_2). The ground state of $Rh_2(CO)_8$ is $...(a_1)^2(a_2)^2(b_2)^2$, and, although the energies of the unoccupied upper orbitals are by no means certain, we envisage a situation of the type depicted in Figure 2. A rich spectrum is predicted for $Rh_2(CO)_8$, as a number of allowed transitions, crudely described as $\sigma \rightarrow \sigma^*$, $d\pi \rightarrow \sigma^*$, and $d \rightarrow \pi$ in nature, should fall below 50 000 cm⁻¹.

Evidence has been presented previously[1b] that suggests that the 282-nm band of bridged $Co_2(CO)_8$ is due to a $\sigma \rightarrow \sigma^*$ transition. It is reasonable, therefore, to associate the intense 260-nm absorption of bridge-bonded $Rh_2(CO)_8$ (Figure 1) with the $\sigma \rightarrow \sigma^*$ transition ($a_1 \rightarrow b_2$ in Figure 2) of the metal–metal bond. That this band *blue-shifts* on passing from $Co_2(CO)_8$ to $Rh_2(CO)_8$ is expected, given the increasing bonding interactions of $\sigma(d)$ orbitals on descending a transition-metal triad.[1c]

The intense, high-energy absorption at 225 nm in the spectrum of $Rh_2(CO)_8$, which *remains* after the disappearance of $Rh(CO)_4$ (as monitored by the characteristic low-energy 320–335-nm $Rh(CO)_4$ band (Figure 1)), is almost certainly attributable to allowed $d\pi \rightarrow \pi$ CO transitions. Not unexpectedly, this absorption system falls very near that of the corresponding MLCT band of $Rh(CO)_4$[4] (Table I).

We note in closing that two relatively weak bands are observed in the $Rh_2(CO)_8$ spectrum (290 and 320 nm, Figure 1). However, in the absence of a more quantitative description of the excited states of bridge-bonded $M_2(CO)_8$ molecules, it would be foolhardy to attempt to assign the weak features to specific transitions. We hope that theoreticians will perform the needed calculations, not only to assist in transition assignments but also to elucidate the detailed electronic makeup of the $a_1b_2(\sigma\sigma^*)$ excited state, whose energy now has been determined both in $Co_2(CO)_8$ and in $Rh_2(CO)_8$ bridged molecules.

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Registry No. $Rh_2(CO)_8$, 29658-60-4; $Rh(CO)_4$, 28132-77-6.

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(3) Note that at -55 °C, $Rh_2(CO)_8$ in its bridge-bonded form disproportionates to $Rh_4(CO)_{12}$, thereby precluding the identification of a "high-temperature nonbridging isomer" of $Rh_2(CO)_8$, analogous to the "low- and high-temperature isomers" of $Co_2(CO)_8$ (see ref 2).
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Contribution from the Elastomers Technology Division, Exxon Chemical Company, Linden, New Jersey 07036,
and the Department of Chemistry, University of California, Los Angeles, California 90024

Crystal Structure, Solubility, and Electronic Spectrum of Titanium Tetraiodide

ERIK G. M. TORNQVIST* and WILLARD F. LIBBY

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The two crystalline forms of TiI_4 and the conditions for their appearance have been studied. The cubic modification belonging to the space group $Pa3$-T_h^6 is apparently always formed when TiI_4 crystallizes from the melt or from a supersaturated solution. However, this modification is metastable at room temperature and converts into a less well-defined structure with a considerably more complicated X-ray diffraction pattern within a period which may vary from a few days to some months, depending upon the size and condition of the crystals in the original cubic modification. The unit cell dimensions of the cubic form determined at 23 °C corresponding to $a_0 = 12.055$ Å were found to differ from those reported previously, in one case quite appreciably. The interplanar *d* spacings for the stable modification also differed slightly from those in the literature, but the exact structure could not be determined. Because of the metastable character of the cubic modification, physical properties of TiI_4, such as solubility in organic solvents, reported in the literature have normally been those of the stable modification. Contrary to literature data, the cubic modification of TiI_4 was found to dissolve very readily and to exhibit appreciable solubility in hydrocarbon solvents. In solution, TiI_4 gives a very interesting electronic spectrum, which is undoubtedly of charge-transfer character and is reminiscent of the one reported for $TiCl_4$ but with the absorptions occurring at considerably higher wavelengths as expected from the much more ready oxidizability of I^- in comparison with Cl^-. Thus the first major absorption for TiI_4 occurs at 517 and 514 nm, in benzene and cyclohexane, respectively, and is responsible for the strong color of this compound. With the established molar extinction coefficients at these wavelengths, the solubility of TiI_4 in benzene and cyclohexane at 23 °C could be determined colorimetrically and was found to be 32.7 and 24.4 g/L, respectively.

Introduction

The crystal structure of TiI_4 was first determined by Hassel and Kringstad,[1] who, for a freshly prepared sample, found it to be cubic and to belong to the space group $Pa3$-T_h^6 and thus to be isomorphous with SnI_4, the lattice of which is built up of tetrahedral molecules. However, a crystal transformation to what appeared to be a less symmetrical modification with a rather complicated X-ray diffraction pattern was observed to take place within a few days, but the structure of this modification was not established. A later investigation by Rolsten and Sisler[2] revealed that TiI_4 prepared by three different methods had a structure similar to the second one reported by Hassel and Kringstad. The observed *d* spacings indexed quite well as a hexagonal lattice, but Rolsten and Sisler were not able to establish a definite structure. However, when heated to 125 °C the TiI_4 was found to undergo a crystal transformation to the cubic structure previously established by Hassel and Kringstad but having a larger cell constant ($a_0 = 12.21$ vs. 12.002 Å) as would be expected from the higher temperature (125 °C vs. room temperature) used for the structure determination.

The solubility of TiI_4 in inert solvents, e.g., hydrocarbons, has not been the subject of much study. However, the few statements in the literature about this property indicate that this compound either is insoluble or has an extremely limited solubility in such solvents.[3-6] The only more definite information on this matter can be found in a paper by Clark and Willis[7] wherein the concentration of a saturated solution in cyclohexane is claimed to be 2.86×10^{-4} M (0.16 g/L) at room temperature. Our interest in TiI_4 developed in connection with Ziegler's discovery of the transition metal containing catalysts now bearing his name, and especially after the disclosure by Zelinski and Smith[8] that TiI_4 in combination with trialkylaluminum will form a very active catalyst for producing high *cis*-1,4-polybutadiene, a novel polymer which exhibited very interesting elastomeric properties. Although an intermediate in the so-called van Arkel–de Boer[9,10] process for purifying titanium, TiI_4 was not at that time a commercially readily available compound, which prompted us to study its synthesis as well as those of its physical properties which could conceivably have a direct bearing on its properties as a polymerization catalyst component. As a result of this study we obtained additional information regarding the conditions under which the two different crystalline modifications of TiI_4 may appear and we also discovered that the solubility of this compound, if properly prepared, may be quite appreciable in hydrocarbons.

Experimental Section

Preparation of TiI_4. This compound was prepared by modifications of two established methods: (1) direct combination of the elements[2] and (2) halogen exchange between $TiCl_4$ and dry HI at a temperature between the melting and the boiling points of the mixture.[1,2,11] In the synthesis according to method (1), 7.2 g (0.15 g-atom) of carefully dried and degassed Ti metal powder (Metal Hydrides, Inc.) was

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* To whom correspondence should be addressed at the Exxon Chemical Co.

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