Registry No. *cis*-$PhMn(CO)_4P(OPh)_3$, 22289-58-3; *trans*-$PhMn(CO)_4P(OPh)_3$, 70397-98-7; $PhMn(CO)_5$, 13985-77-8.

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Electronic Absorption Spectra of Metal Tetracarbonyls

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The electronic absorption spectra of approximately tetrahedral $M(CO)_4$ (M = Ni, Pd, Pt, Co, Rh, Ir) molecules have been measured. The closed-shell molecules (M = Ni, Pd, Pt) exhibit d → π^* CO bands in the ultraviolet region of the spectrum. The band at 36 630 cm^{-1} in the spectrum of $Ni(CO)_4$ is assigned to $t_2(d) \rightarrow t_2(\pi^*)$, and the broad system at 41 670 cm^{-1} probably represents several other d → π^* transitions. Similar bands are observed at slightly higher energies in the spectrum of $Pd(CO)_4$. The spectrum of $Pt(CO)_4$ shows a single band at 48 310 cm^{-1}, which is attributed to a d → p or d → π^* transition. Relatively low-energy $\sigma \rightarrow t_2(d)$ transitions are observed in the spectra of the open-shell molecules (28 190, 28 900, 31 720 cm^{-1} in $Co(CO)_4$; 29 850 cm^{-1} in $Rh(CO)_4$; 32 570 cm^{-1} in $Ir(CO)_4$). Transitions with d → π^* character are observed at 37 180, 39 060, and 44 840 cm^{-1} in $Co(CO)_4$, 41 670 and 46 510 cm^{-1} in $Rh(CO)_4$, and 40 650 and 48 080 cm^{-1} in $Ir(CO)_4$.

Introduction

It has been known for several years that metal carbonyl complexes possess relatively low-lying excited states of the metal-to-ligand charge-transfer (MLCT) type. The most extensive investigations of the electronic spectra have been performed on metal hexacarbonyls,[2,3] although other systems have been studied in a less detailed fashion.[4] The recent characterization of $M(CO)_4$ molecules in matrix-isolation experiments[5,6] has allowed us to probe the electronic energy levels of approximately tetrahedral closed-shell (M = Ni, Pd, Pt)[5] and open-shell (M = Co, Rh, Ir)[6] molecules. The electronic spectra of metal carbonyl molecules with open-shell ground states have turned out to be of special interest, as we have observed low-lying ligand-to-metal charge transitions (LMCT) in these cases.

Experimental Section

Monoatomic metal vapors of Ni, Co, and Rh were generated by directly heating thin ribbon filaments (0.010 in.) with an alternating current. For the other metals, Pd (0.005 in. foil), Pt (0.020 in. wire), and Ir (0.010 in. wire) were wound around a tungsten rod (0.030 in.

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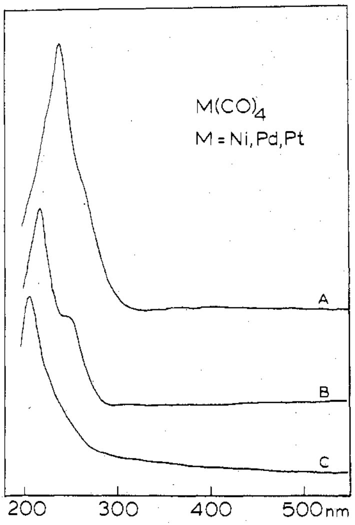

Figure 1. Matrix spectra (200–500 nm) of the products of (A) Ni/CO $\simeq 1/10^4$, (B) Pd/CO $\simeq 1/10^4$, and (C) Pt/CO $\simeq 1/10^4$ cocondensation reactions at 12 K.

Table I. Electronic Spectral Data for $M(CO)_4$ Molecules

M	band positions, cm^{-1}	assignt
Ni	36 630 sh	$t_2(d) \rightarrow t_2(\pi^*)$
	41 670	$d \rightarrow \pi^*$
Pd	40 000 sh	$t_2(d) \rightarrow t_2(\pi^*)$
	45 870	$d \rightarrow \pi^*$
Pt	48 310	$d \rightarrow p$ or $d \rightarrow \pi^*$
Co	28 190	$\sigma \rightarrow t_2(d)$
	28 900 sh	$\sigma \rightarrow t_2(d)$
	31 720	$\sigma \rightarrow t_2(d)$
	37 180 sh	$d \rightarrow \pi^*$
	39 060	$d \rightarrow \pi^*$
	44 840	$d \rightarrow \pi^*$
Rh[a]	29 850	$\sigma \rightarrow t_2(d)$
	41 670	$d \rightarrow \pi^*$
	46 510	$d \rightarrow \pi^*$
Ir	32 570	$\sigma \rightarrow t_2(d)$
	40 650 sh	$d \rightarrow \pi^*$
	48 080 sh	$d \rightarrow \pi^*$

[a] $Rh(CO)_4$ bands displayed slight matrix-concentration and temperature-dependent energy shifts.

diameter) and directly heated. All metals were supplied by A. D. Mackay Inc., New York, N.Y. Research grade $^{12}C^{16}O$ (99.99%) was obtained from Matheson of Canada.

A description of the furnace used for metal evaporation and details of the method for monitoring the rate of metal atom depositions have been reported previously.[7]

Matrices were deposited on a NaCl optical plate cooled to 10–12 K by an Air Products Displex closed-cycle helium refrigerator. All UV–visible absorption spectra were recorded with either a Varian Techtron 635 or a Unicam SP 8000 spectrophotometer.

For the formation of the various tetracarbonyl species, matrix gas flows of pure CO were maintained at 1 mol/h. To ensure formation of the mononuclear complexes and minimize binuclear complex formation, the metal-to-matrix gas ratio was $M/CO \leq 1/10^4$ for M = Ni, Pd, Pt, Co, Rh, and Ir. Under these conditions, spectroscopically pure $M(CO)_4$ species were generated and stoichiometrically characterized by mixed $^{12}C^{16}O/^{13}C^{16}O$ or $^{12}C^{16}O/^{12}C^{18}O$ infrared isotopic substitution experiments.[5,6,8,9]

Results and Discussion

$Ni(CO)_4$, $Pd(CO)_4$, and $Pt(CO)_4$. Each of these species exhibits a single intense absorption band in the ultraviolet region of the spectrum with, in the case of nickel and palladium, a well-pronounced shoulder 5000–6000 cm^{-1} to lower energy (Figure 1, Table I). There is no evidence of a shoulder in the spectrum of $Pt(CO)_4$.

There have been several molecular orbital treatments of nickel carbonyl,[10–18] and the photoelectron spectrum of the molecule has also been reported.[13,14,19] Although there are differences in detail, there is general agreement that the highest filled orbitals are e and t_2 of the d manifold, split by about 5000 cm^{-1}, with the latter at higher energy. The next level is primarily composed of the t_2 σ-bonding orbitals of the carbonyl groups and lies about 35 000 cm^{-1} below the filled e orbitals. Transitions from this level are not expected below 50 000 cm^{-1}. The lowest unoccupied orbitals are derived from π^*CO levels and are t_2, e, and t_1 (Figure 2).

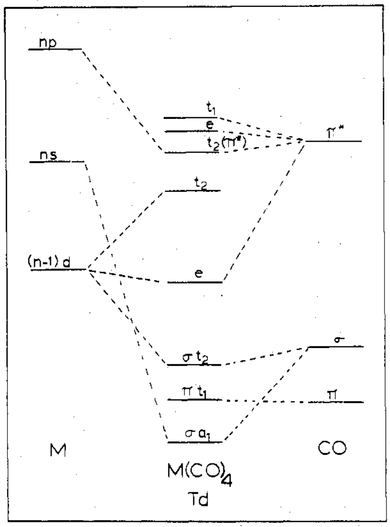

Figure 2. Qualitative molecular orbital energy level scheme for $M(CO)_4$ complexes of T_d symmetry. MO levels of π symmetry below πt_1 are not shown.

We propose that the low-energy shoulder in $Ni(CO)_4$ and $Pd(CO)_4$ be assigned to $t_2(d) \rightarrow t_2(\pi^*)$, as the latter orbitals should be stabilized by mixing with metal p functions. The intense band at higher energy probably represents several overlapping transitions with $t_2(d) \rightarrow \pi^*$ and $e(d) \rightarrow \pi^*$ character. It is not possible to assign the spectrum in any more detail with the information at hand.

The apparent absence of the low-energy shoulder in the $Pt(CO)_4$ spectrum may mean that the $t_2(d) \rightarrow t_2(\pi^*)$ transition has shifted to higher energy. Indeed, the band at 48 310 cm^{-1} may represent $t_2(d) \rightarrow t_2(\pi^*)$. Alternatively, the 48 310-cm^{-1} band could be primarily a $d \rightarrow p$ type transition, $e(d) \rightarrow t_2$. Such $d \rightarrow p$ transitions are often observed in the ultraviolet spectra of platinum complexes.[3]

$Co(CO)_4$, $Rh(CO)_4$, and $Ir(CO)_4$. Whereas the complexes described above are closed-shell, 18-electron, regular tetrahedral species, the cobalt series possess only 17 valence electrons and are not expected to be regularly shaped. Infrared and electron spin resonance spectral data reveal that $Co(CO)_4$ has a marked C_{3v} distortion.[8,20] The other two complexes, however, appear to be approximately tetrahedral. The cobalt complex has a spectrum (Figure 3) that is more complex than that observed for either the rhodium or the iridium analogue (Figure 4). There is a splitting of the principal ultraviolet bands of roughly 2000 cm^{-1}, whereas the pair of near-ultraviolet bands are separated by nearly 3000 cm^{-1}, with the lower energy band revealing a shoulder. Fewer features are clear in the spectra of $Rh(CO)_4$ and $Ir(CO)_4$. However, the lower energy band in the spectrum of $Rh(CO)_4$ is very broad and could readily encompass several transitions. The low-energy band of $Ir(CO)_4$ is similarly broad, and the rising edge of the high-energy system exhibits shoulders. Band positions are given in Table I.

On the basis of the assignments of the MLCT bands in the $Ni(CO)_4$ family, the ultraviolet absorptions in the open-shell $M(CO)_4$ complexes are attributed to $d \rightarrow \pi^*$ transitions. The low-energy features, which are not observed in the closed-shell

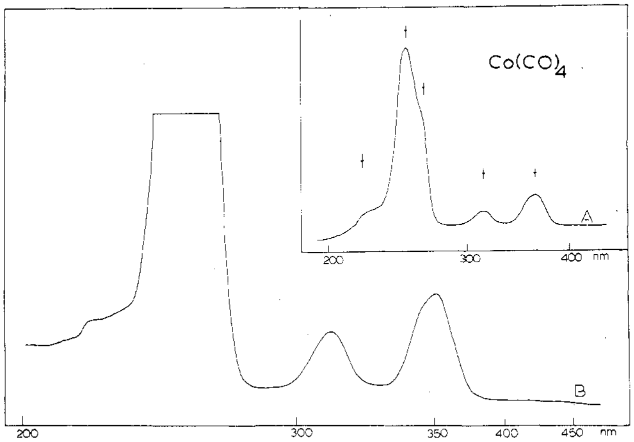

Figure 3. Matrix spectra (200–500 nm) of the product of a Co/CO $\simeq 1/10^4$ cocondensation reaction at 12 K. Note that B is a scale expansion of A and that a scale change occurs between 300 and 400 nm.

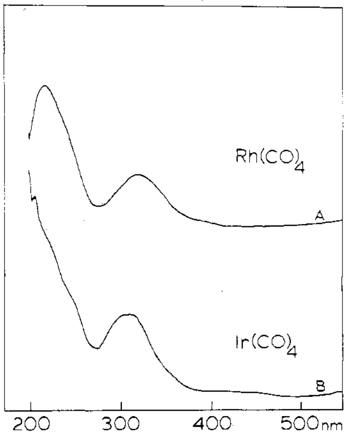

Figure 4. Matrix spectra (200–500 nm) of the products of (A) Rh/CO $\simeq 1/10^4$ and (B) Ir/CO $\simeq 1/10^4$ cocondensation reactions at 12 K.

molecules, fall over 10 000 cm^{-1} below the main MLCT band in each case. It is not likely that these bands are d–d transitions,[8] as this would imply unacceptably large splittings of the e(d) and t$_2$(d) levels. It is possible that the low-energy bands are MLCT transitions, but we prefer an alternative interpretation, namely, that they be assigned to $\sigma \rightarrow t_2$(d), the latter being LMCT transitions from bonding σ-carbonyl levels into the hole in the t$_2$ set on the metal. The energy separation between the σ and t$_2$(d) levels in Ni(CO)$_4$ may be estimated to be about 42 000 cm^{-1} from the photoelectron spectrum.[13] The $\sigma \rightarrow t_2$(d) transition in the cobalt series is expected to occur well below 42 000 cm^{-1}, as a closed d shell is formed in the excited state. Thus it is quite reasonable to assign bands near 30 000 cm^{-1} to such LMCT transitions.[21]

The σ orbitals are likely to be perturbed in the lower (C_{3v}) symmetry of the cobalt complex to a much greater degree than the π^* set. For this reason we assign the near-ultraviolet bands in Co(CO)$_4$ (ground state $^2A_1$ in C_{3v} symmetry)[8,20] to the LMCT transitions $^2A_1 \rightarrow {}^2A_1$ and $^2A_1 \rightarrow {}^2E$. The higher intensity and slight splitting observed in the lower energy band are consistent with its assignment to the latter transition.

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Registry No. Ni(CO)$_4$, 13463-39-3; Pd(CO)$_4$, 36344-80-6; Pt(CO)$_4$, 36344-81-7; Co(CO)$_4$, 58207-38-8; Rh(CO)$_4$, 28132-77-6; Ir(CO)$_4$, 28132-78-7.

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