$H_5)_2CH_3]Cl$, 69120-69-0; $(C_6H_5)_3C_3Ni[P(C_6H_5)Cl_2]_2Cl$, 69120-70-3; $(C_6H_5)_3C_3Ni[P(OC_6H_5)_3]Cl$, 69120-71-4; $(C_6H_5)_3C_3Ni[P(C_6H_5)Cl_2]Cl$, 69120-72-5; $(C_6H_5)_3C_3Ni[P(C_6H_5)_2Cl]Cl$, 69120-73-6; $(C_6H_5)_3C_3Ni[P(OCH(CH_3)_2)_3]Cl$, 69120-74-7; $(C_6H_5)_3C_3Ni[P(OCH_3)_3]Cl$, 69120-75-8; $(C_6H_5)_3C_3Ni[P(C_6H_5)_2Cl]_2Cl$, 69120-73-6; $(C_6H_5)_3C_3Ni[P(C_6H_5)_2CH_3]_2Cl$, 69177-57-7; $(C_6H_5)_3C_3Ni[P(OC_6H_5)_3]_3Cl$, 69120-76-9; $(C_6H_5)_3C_3Ni[P(C_6H_5)Cl_2]_3Cl$, 69120-77-0; $(C_6H_5)_3C_3Ni[P(C_6H_5)_2Cl]_3Cl$, 69120-78-1; $(C_6H_5)_3C_3Ni[P(OCH(CH_3)_2)_3]_3Cl$, 69120-79-2; $(C_6H_5)_3C_3Ni[P(OCH_3)_3]_3Cl$, 69120-80-5.

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# UV Photoelectron Study of Mononuclear Metal Complexes of Methylaminobis(difluorophosphine)

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Gas-phase UV photoelectron spectra are reported of the title ligand L, of its mononuclear $ML_3$ complexes (M = Cr, Mo, W), and of the polynuclear Ni and Rh complexes. Ionization of the $d^6$ system of $ML_3$ occurs at relatively low IE between ca. 7.7 and 7.9 eV. An assignment is proposed for the higher ionization processes, covering coordinative $\sigma_{MP}$, N lone pair, $\sigma_{CH}$ and $\sigma_{NP}$, and fluorine $\sigma$ and $\pi$ orbitals.

## Introduction

The mononuclear tris-chelate complexes of the $d^6$ metals Cr, Mo, and W with methylaminobis(difluorophosphine) (L), first reported[1] in 1977, and the polynuclear complexes of Ni and Rh have been investigated by UV photoelectron spectroscopy in the gas phase. Their spectra are generally well resolved and yield clear, even if not always detailed, information about the electronic structure of the valence shell, including the energy position of metal d orbitals, of the $\sigma$-bonding coordination orbitals, and of the electron lone pairs present in the ligand structure. Comparisons and structural correlations can be drawn and will be discussed in the next sections, with other volatile complexes of zerovalent metals, particularly with carbonyls and $PF_3$ complexes of $d^6$ elements.

## Experimental Section

The free ligand $CH_3N(PF_2)_2$ is a highly volatile liquid,[2] and its photoelectronic spectrum was recorded from liquid samples. $CrL_3$, $MoL_3$, $WL_3$, $[NiL_2]_n$, and $Rh_4L_6$ were prepared according to previous literature reports[1,4] and proved sufficiently volatile for measurements as solid samples in the photoelectron spectrometer. For the Ni compound, "$n$" is known to be predominantly 2 in the gas phase from mass spectral measurements.[3] Approximate temperatures required to obtain spectra of good intensity at the internal pressure of the spectrometer were 60 °C for $CrL_3$, 65–70 °C for $MoL_3$, 90 °C for $WL_3$, 125 °C for $[NiL_2]_n$, and 210 °C for $Rh_4L_6$. The Cr, Mo, and W compounds appeared to be completely stable, leaving no residue after sublimation; and are assumed to be present in the gas phase in the same mononuclear pseudooctahedral structure assigned to them in the solid state. The Ni and Rh complexes are accompanied by consistent traces of water and left decomposed, solid residues after photoelectronic measurements.

Photoelectronic spectra were taken on a Perkin-Elmer PS 18 photoelectron spectrometer with the use of He I 584-Å radiation in the presence of Ar and $CH_3I$ as calibrant gases. The Cr and W complexes were also measured with He II 304-Å radiation, which however does not produce in the present case any remarkable change in the peak intensity. Reproducibility of the spectra was in any case excellent, provided the temperature, whose effect is critical, was kept constant to better than ca. 2 °C; instrumental resolution was typically 40 meV at the Ar doublet energy (15.76–15.94 eV IE). All substances exerted a moderate attack on the internal walls of the spectrometer, resulting in slight contamination after each run.

## Results

The free ligand $CH_3N(PF_2)_2$ has, in the low IE region, a composite band with maximum at 10.95 and shoulder at 11.45 eV (approximate intensity ratio 2:1) that is in the region where ionization of the lone pairs of N and P are expected (see Table I and Figure 1). The ionization of the P lone pairs appears at 12.31 eV in $PF_3$ and 10.50 eV in $(CH_3)_2N{-}PF_2$.[6,7] Since the electronegativity of the surrounding groups around P is very similar in $(CH_3)_2N{-}PF_2$ and $CH_3N(PF_2)_2$, and just slightly larger in the latter case, assignment of the 10.95-eV band component in $CH_3N(PF_2)_2$ to $n_P$ seems plausible. The N lone-pair ionization in $(CH_3)_2N{-}PF_2$ is at 9.60 eV but is expected to shift considerably to higher values in $CH_3N(PF_2)_2$, where nitrogen has two highly electronegative $-PF_2$ neighbors instead of one and can thus be identified as the 11.45-eV component.

Another support to this assignment comes from the comparison with $NH_2{-}PF_2$, whose UV PES is reported and assigned in ref 7. This spectrum has two bands in the energy region of the N and P lone pairs which the authors[7] relate in order of increasing energy to the $n_N$, at 10.7 eV (this vertical IE is the same as in $NH_3$), and to the $n_P$, at 11.5 eV, on the grounds of the fact that the two lone pairs do not interact, being orthogonal to each other. We propose an alternative assignment, where the IE of the N lone pair is instead identified with the 11.5-eV band, i.e., at a higher value with respect to $NH_3$, due to the $-PF_2$ group being more electronegative than the H atom and exerting its inductive effect even if the N and P lone pairs do not interact directly.

This implies a reverse order of energy levels, with the $n_P^{-1}$ ionization at 10.9 eV and the $n_N^{-1}$ at 11.5 eV. Now these values are equal to those proposed by us for the $n_N$ and $n_P$ ionizations of the $(PF_2)_2NCH_3$ molecule, which implies that the $-PF_2$ and $-CH_3$ groups, which replace two H atoms in

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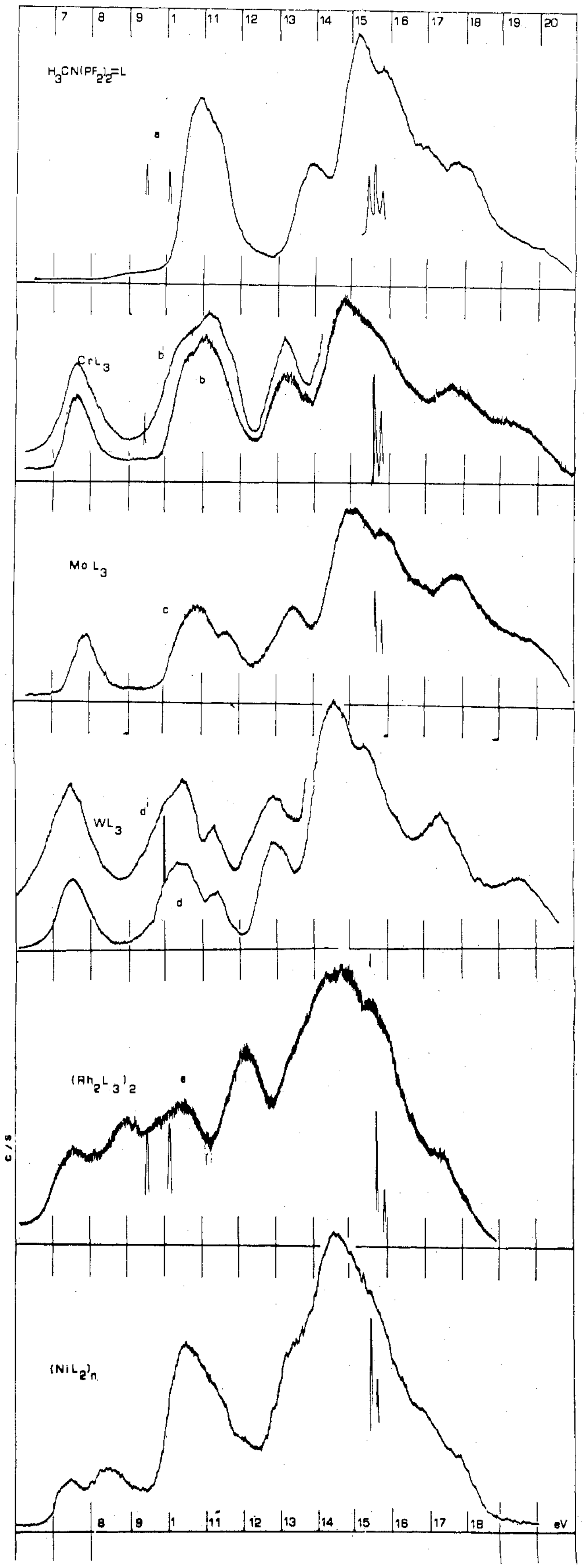

**Figure 1.** He I photoelectron spectra of (a) $H_3CN(PF_2)_2$ (=L), (b) $CrL_3$, (c) $MoL_3$, (d) $WL_3$, (e) $Rh_4L_6$, and (f) $NiL_2$; (b′) and (d′) are He II spectra.

$PF_2$–$NH_2$, introduce opposite inductive effects of approximately equal magnitude.

In the IE region above ~15.5 eV, the photoelectronic spectrum of the free ligand has several partly resolved maxima; the maxima or shoulders at 15.99, 17.09, and 17.99 eV are very close in shape and energy to the photoelectronic spectral patterns exhibited by $PF_3$[5] (at 15.91, 17.54, and 18.54 eV) and by several other P–F compounds[6–10] and are assigned to the ionization of the lone pairs, or $\pi_F$ fluorine orbitals, while the 20.29-eV band could be one of the $\sigma_{PF}$ ionizations. The two bands with maxima at 14.05 and 15.34 eV should account for ionization of the remaining molecular orbitals on the basis of atomic p orbitals present in the valence shell of the ligand, and in particular for at least one of the (N–C + N–P) $\sigma$ bonds, and for two of the three C–H $\sigma$ bonds ("e" component in the local trigonal symmetry of the methyl group). At the present stage it is not possible to decide with certainty about the actual assignment of each band also because the low molecular symmetry allows mixing between both types of bond orbitals. Comparison with $PF_2$–$NH_2$,[7] having no band between 12 and 14.5 eV, suggests that the band at 14.05 eV could be associated to a MO with main contributions from $\sigma_{CH}$ and the 15.39-eV band to an orbital of predominant $\sigma_{CN}$ character.

The UV PES of mononuclear $CrL_3$, $MoL_3$, and $WL_3$, which are assumed to have pseudooctahedral structure in the gas phase, retain all gross features of the photoelectronic spectrum of free L, except for (i) appearance of an extra band at low IE with maxima around 7.7–8.0 eV, (ii) broadening and different shape of the composite band in the region between ca. 11 and 12 eV, and (iii) small quantitative shifts and changes in shape of the band system beyond ca. 15 eV, to which we attach less significance.

(i) The extra band at 7.70 eV in $CrL_3$ and $WL_3$ and at 7.93 eV in $MoL_3$ can only be due to the $d^6$ configuration of the central metal. It is evidently not split, although both the trigonal symmetry of the complexes ($t_{2g} \rightarrow e + a_2$) and the spin–orbit coupling effects (expected to be particularly strong in the W compound) should lead to splitting into at least two components. Actually the splitting is small, if any, since it is contained within the observed bandwidth of 0.7–0.8 eV, which is of the same order of magnitude as observed in the truly octahedral complexes of the same $d^6$ metals with CO[11,12] or $PF_3$.[13,14] The IE values for d ionization in the complexes of $CH_3N(PF_2)_2$ are much lower than in the corresponding complexes of $PF_3$, a fact in line with the presence of less electronegative moieties in the former ligand, and are even lower than in the corresponding metal carbonyls, which surprisingly reflects the slightly smaller overall electron-withdrawing ability of $CH_3N(PF_2)_2$ with respect to CO. Furthermore, in our series we do not observe the increase of IE of the "d" orbital, which, according to Nixon[14] is expected on moving from first- to third-row complexes. The constancy of the $t_{2g}$ energy has also been found for the analogous $PF_3$ complexes by Nixon and co-workers.[14]

(ii) The $n_P$ orbitals are expected to become $\sigma$ bonding in the coordination sphere, hence to shift to lower orbital energies, or higher IE, and to split to some extent ($6n_P \rightarrow a_{1g} + e_g + t_{1u}$ in the octahedral limit), while remaining still in the same energy region as the $n_N$ lone pairs and probably intermixed with them. Actually there is only a very small shift, if any, of the center of gravity of the involved band system to lower orbital energies on complexation; a similar tendency was already observed in the ESCA of several phosphine complexes,[15] where phosphorus 2p binding energies do not change appreciably from free to complexed phosphines, a fact attributed to a balance between $\sigma$-donor and $\pi$-acceptor effects on phosphorus.[15] This situation contrasts to some extent with that of the metal complexes of $PF_3$,[13,14] where the $n_P$ ionizations

**Table I.** Vertical Ionization Energies (eV) in the Photoelectronic Spectra of Zerovalent Transition-Metal Phosphine Complexes[a]

| compd | $nd^6$ | $n_N + (n_P \text{ or } \sigma_{MP})$ | $\sigma_{CH} + \sigma_{CN}$ | $\pi_F + \sigma_{PF}$ |
|---|---|---|---|---|
| $PF_3$* | | 12.31 | | 15.91–17.45–18.54–19.5 |
| $(H_3C)_2NPF_2$* | | 9.60–(10.50) | 14.35 | 16.55–17.20 |
| $H_3CN(PF_2)_2$ = L | | 10.95–11.45<br>[[1.26]] | 14.05–15.34 | (15.99)–17.09–17.95–20.3 |
| $CrL_3$ | 7.70<br>[1.00] [[0.77]] | (10.76)–11.20<br>[3.47] [[1.47]] | 13.40–15.20 | (15.80)–17.86–20.40 |
| $Cr(PF_3)_6$* | 9.29 | 12.84 | | 15.80–17.36–19.3 |
| $Cr(CO)_6$* | 8.40 | | | |
| $MoL_3$ | 7.93<br>[1.00] [[0.76]] | 10.97–11.80<br>[3.00] [[1.66]] | 13.50–15.20 | 15.93–17.96–20.0 |
| $Mo(PF_3)_6$* | 9.17 | 12.94–13.48–13.93 | | 15.80–17.36–19.1 |
| $Mo(CO)_6$* | 8.50 | | | |
| $WL_3$ | 7.70<br>[1.00] [[0.80]] | 11.02–11.94<br>[2.37] [[1.90]] | 13.52–15.14 | (16.10)–18.00–20.20 |
| $W(PF_3)_6$* | 9.30 | 12.26–12.64–13.52 | | 15.85–17.44–18.7 |
| $W(CO)_6$* | 8.56 | | | |
| $Rh_4L_6$** | 7.50–8.95<br>[1.00] [[>2.6]] | 10.40–12.18<br>[>2.0] [[>3.0]] | (13.4)–14.62 | (15.60)–(17.35) |
| $[NiL_2]_n$** | 7.65–8.65<br>[1.00] [[>2.2]] | 10.70–(11.4)<br>[1.96] [[1.76]] | (13.65)–14.80 | (15.80)–(17.50) |

[a] * = data from the literature. [b] ** = $d^9$ for each Rh or $d^{10}$ for each Ni. [c] [ ] = approximate intensity ratios, uncorrected. [d] [[ ]] = full width at half-maximum (eV).

are shifted by as much as 0.5–1.0 eV to higher IE on complexation; evidently in complexes of $CH_3N(PF_2)_2$ the methylamine group is better able to compensate any tendency to increase the positive charge on the phosphorus atom, possibly by way of $p_N \rightarrow d_P$ bond formation. The shape of the band system varies from metal to metal, and also, if the individual components of the $(\sigma_{MP} + n_N)$ set cannot be singly identified, we note for $CrL_3$ just one composite band with maximum at ~11 eV and for $MoL_3$ and $WL_3$ two bands, the second of which is smaller and occurs at higher IE values, i.e., at 11.8–11.94 eV.

This fact agrees with findings in other phosphine complexes[14] and confirms that the ionizations of energy levels derived from M–P σ bonds of the first-row transition-metal complexes are contained in one band of their photoelectronic spectrum, while second- and third-row metal complexes give rise to a series of bands, which move to higher IE's.

It is interesting to compare the analogous M–$PF_3$ complexes: the center of gravity of the $\sigma_{MP}$ levels is shifted more evidently to higher IE in the latter compounds, and this splitting is reported variably from ~1 eV in $Ni(PF_3)_4$[11,12] to nearly 3 eV in $Pt(PF_3)_4$.[13,14] Our present data suggest a not very large splitting.

The polymeric nickel compound $[NiL_2]_n$ is possibly decomposed on sublimation in the photoelectron spectrometer and leaves a nonvolatile residue. However, the photoelectronic spectrum of the volatile fraction, for which mass spectral data suggest a prevailing dimeric structure, is neat, reproducible, and fairly similar to those of the remaining complexes of L; also, the intensity ratio of the d ionization bands to the $(\sigma_{MP} + n_N)$ ionization bands is roughly in agreement with a 1:2 metal-to-ligand ratio as in the polymeric starting material. The profile and energy position of the bands in the $(\sigma_{MP} + n_N)$ region (maximum at 10.70, shoulder around 11.6 eV), and in the whole pattern in the region above 13 eV, are very similar, e.g., to those of $MoL_3$ and $WL_3$. The d-ionization region is of particular interest since it corresponds to the photoionization of a polynuclear transition-metal chromophore, of which there are not many examples in UV PES literature.[16,17] There is here a broad sequence of bands, with two more pronounced maxima (7.65 and 8.65 eV, in approximate intensity ratio 2:3), still clearly separated from the $(\sigma_{MP} + n_N)$ ionizations. No evidence is available as yet on the coordination geometry and bond structure of Ni in the vapor-phase, dimeric form of the compound; a tetrahedral arrangement of donor $PF_2$ groups around each nickel atom as in $Ni(PF_3)_4$ would require a 3:2 instead of 2:3 intensity ratio, and it therefore appears unlikely unless distorted by involving one of the $dt_2$ orbitals in metal–metal bonding.

The rhodium complex $Rh_4L_6$ is again comparable to the mononuclear, group 6 tris chelates. The d ionizations occur in a broader region, with two prominent maxima 1.45 eV apart, plus a possible third one intermixed with the $(\sigma_{MP} + n_N)$ ionizations. The d region is therefore no longer sharply separated from the latter region; an approximate estimate of intensities indicates a higher intensity ratio to the $(\sigma_{MP} + n_N)$ ionizations than in the other complexes of the same ligand, in agreement with the lower ligand-to-metal ratio (36 d electrons:36 $(n_P + n_N)$ electrons in $Rh_4L_6$; compare, e.g., 6:18 in $CrL_3$). More detailed assignment will be possible once the actual structure of the polynuclear entity is known, the photoelectronic spectral patterns in this region being potentially informative about metal–metal interactions in the polynuclear entity. The $(\sigma_{MP} + n_N)$ region exhibits two main bands, more apart (10.40 and 12.18 eV) than in the other complexes of L. The region of higher IE shows only a small (~0.2 eV) shift to lower values with respect to all other complexes reported in this work.

**Registry No.** $Cr(CH_3N(PF_2)_2)_3$, 63404-40-0; $Mo(CH_3N(PF_2)_2)_3$, 63353-75-3; $W(CH_3N(PF_2)_2)_3$, 63371-85-7; $[Ni(CH_3N(PF_2)_2)_2]_n$, 66632-67-5; $Rh_4(CH_3N(PF_2)_2)_6$, 66687-72-7; $CH_3N(PF_2)_2$, 17648-18-9.

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# Reaction of Chelating Ligands with Tetracarbonylnickel, Nitrosyltricarbonylcobalt, and Dinitrosyldicarbonyliron: A Kinetics Study

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The kinetics of the interactions of several chelating ligands with $Ni(CO)_4$, $CoNO(CO)_3$, and $Fe(NO)_2(CO)_2$ are examined. In all cases, two molecules of CO are evolved, being replaced by the ligand. $Ni(CO)_4$ reacts with 1,10-phenanthroline (phen), *o*-phenylenebis(dimethylarsine) (DAS), *cis*-1,2-bis(dimethylarsino)ethylene (EDAS), and 1,2-bis(diphenylarsino)ethane (diars) in two consecutive, first-order reactions. The first is a dissociation of CO to give the intermediate $Ni(CO)_3$ which is rapidly attacked by one of the donor atoms of the chelate. The rate of this reaction is independent of the nature and concentration of the incoming ligand. The second reaction is first order but associatively activated and involves the displacement of a second CO ligand by the unattached donor atom of the chelating ligand. The rate of ring closure increases with the basicity of that atom, but steric influences may be important. For $CoNO(CO)_3$ and $Fe(NO)_2(CO)_2$, the ring closure reaction is not kinetically accessible, since the attachment of the first donor atom is rate determining. This reaction for $CoNO(CO)_3$ exhibits mixed first- and second-order kinetics (rate = $(R_1 + R_2[AA])[CoNO(CO)_3]$), the former resulting from the intervention of a solvent path to product. $Fe(NO)_2(CO)_2$ reacts with phen by a purely second-order associative path, but the arsines prove to give reactions poorly suited to kinetics analysis.

## Introduction

Numerous kinetic studies have been carried out of a bidentate ligand replacing two monodentate ligands bound to a metal atom. In the majority of cases, the closing of the chelate ring was not detected kinetically.[1-18] The energetics of the second step of substitution was similar to that of the first, but the probability for ring closure was much greater than the probability of the initial step of substitution, so that the substitution step (or some earlier step on the route to product) was rate determining for the overall reaction, and the second was kinetically inaccessible. The increased probability of the reaction has been interpreted as a very high effective concentration of the unbound end of the ligand.

Some ring closures have been followed kinetically. In one case,[19] the dangling end of an ethylenediamine ligand was prevented from becoming bound to platinum(II) by protonation; the reaction proceeded when the pH was raised. Alternatively, some first steps of substitution by potential chelates render the metal center sufficiently inert to further substitution that the reaction stops, and ring closure can be observed only by raising the temperature.[20-23] Some indirect observations of ring closures have been made,[24] but the complexity of the systems has precluded calculation of the rate constant.

Ring-closure studies can in some cases be used to evaluate the effective concentration of the dangling end of the chelate by comparing the rate of the reaction to that of a second step of substitution by a similarly nucleophilic monodentate ligand. Carter and Beattie, although they observed a ring-closing rate about 1000 times faster than substitution in the absence of a chelate effect, assigned only a 30-fold enhancement factor to the high "virtual concentration".[19] Angelici,[25] on the other hand, interpreting some results of Basolo[20] on nitrosyltricarbonylcobalt, calculated an effective concentration of 500 M.

Phosphorus chelates appear to confer on the metal center of the iron and cobalt compounds too great a degree of inertness to make it convenient to study both substitution and ring closure under the same conditions. In this paper we report some studies with nitrogen and arsenic chelates (AA).

## Experimental Section

**Materials.** Tetracarbonylnickel, $Ni(CO)_4$, was purchased from Strem Chemicals, Inc., and used without further purification. Nitrosyltricarbonylcobalt, $CoNO(CO)_3$, and dinitrosyldicarbonyliron, $Fe(NO)_2(CO)_2$, were prepared according to literature procedures[26,27] and purified by trap-to-trap distillation in a vacuum line. They were stored in foil-wrapped ampules at −78 °C prior to use. 1,10-Phenanthroline monohydrate,[28] $C_{12}H_8N_2{\cdot}H_2O$, was dehydrated by heating for 24 h at 80 °C under vacuum; mp 117 °C (lit.[29] mp 117 °C). *o*-Phenylenebis(dimethylarsine),[30] $C_6H_4[As(CH_3)_2]_2$, and *cis*-1,2-bis(dimethylarsino)ethylene,[31] $(CH_3)_2AsCH{=}CHAs(CH_3)_2$, were vacuum distilled prior to use. 1,2-Bis(diphenylarsino)ethane,[32] $(C_6H_5)_2AsCH_2CH_2As(C_6H_5)$, was recrystallized twice from ethanol; mp 96–99 °C (lit.[32] mp 100–101 °C). *o*-Xylene, $C_6H_4(CH_3)_2$, and decalin, $C_{10}H_{18}$, were AR grade. They were allowed to stand over 4-Å molecular sieves for several days, were distilled in a nitrogen atmosphere, and were stored with sieves under nitrogen.

**Kinetics Studies.** Reactions were run in all-glass vessels that included effectively constant-volume manometers. Reagent solutions were loaded in an inert-atmosphere box, thermostated in a constant-temperature bath, and then mixed. The progress of the reaction was monitored by measuring the rise in carbon monoxide pressure. Since rates were light sensitive, the reaction vessels were wrapped in foil.

Most kinetics runs were carried out under pseudo-first-order conditions with at least a sixfold excess of ligand and were followed to at least 70% completion. Final carbon monoxide pressures were used to determine the stoichiometry of the reaction. Reaction products were identified by their infrared spectra.

For reactions with iron and cobalt compounds, standard procedures were used to obtain observed first-order rate constants from the pressure data under pseudo-first-order conditions. Second-order rate constants were calculated from graphs of $k_{obsd}$ plotted as functions of ligand concentrations. Visual line-fitting and least-squares calculations agreed. Tetracarbonylnickel exhibited kinetics indicating two consecutive, first-order reactions with comparable rate constants, $k_1$ and $k_1'$, which were separated by a graphical method devised by Swain.[33]