

Reactivity of Formaldehyde and Acetaldehyde toward $[\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3]\text{Ni}$ and $[\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3]\text{CoH}$

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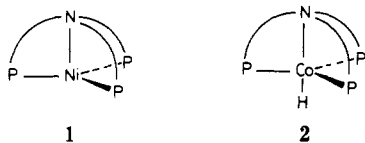
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The Ni(0) complex $(\text{np}_3)\text{Ni}$ [$\text{np}_3 = \text{tris}(2\text{-}(\text{diphenylphosphino})\text{ethyl})\text{amine}$] reacts with formaldehyde to give the paramagnetic Ni(I) formyl complex $(\text{np}_3)\text{Ni}(\text{CHO})$, which decomposes to the diamagnetic Ni(0) carbonyl $(\text{np}_3)\text{Ni}(\text{CO})$. Formaldehyde reacts with the Co(I) hydride $(\text{np}_3)\text{CoH}$ or with the methyl complex $(\text{np}_3)\text{Co}(\text{CH}_3)$ to give the hydrido carbonyl compound $(\text{np}_3)\text{Co}(\text{CO})\text{H}$. When the latter reactions are carried out in the presence of NaBPh_4 , the cationic carbonyl $[(\text{np}_3)\text{Co}(\text{CO})]\text{BPh}_4$ is formed. Acetaldehyde and propionaldehyde react with $(\text{np}_3)\text{CoH}$ yielding the corresponding paramagnetic η^1 -acyl complexes $(\text{np}_3)\text{Co}(\text{COCH}_3)$ and $(\text{np}_3)\text{Co}(\text{COC}_2\text{H}_5)$. The reactivity of the acetyl derivative toward nucleophiles and electrophiles is investigated. Nucleophiles displace the acetyl ligand to give the corresponding complexes $(\text{np}_3)\text{Co}(\text{Nu})$, whereas electrophiles remove the acetyl ligand to give the $[(\text{np}_3)\text{Co}]^+$ moiety. Possible reaction mechanisms are suggested on the basis of chemical and theoretical data.

Introduction

Much current interest in the organometallic chemistry of formaldehyde stems from the key roles that the $\text{M}(\text{CH}_2\text{O})$ fragment and the related $\text{M}(\text{CHO})$ and $\text{M}(\text{CO})\text{H}$ fragments seem to play in metal-assisted carbon monoxide reduction.¹ Few reactions of transition-metal complexes with formaldehyde, however, have been reported so far (Scheme I). In most instances, the reaction of a metal complex with formaldehyde gives $\eta^2\text{-H}_2\text{CO}$ complexes,² or metal carbonyls,³ whereas the bottom three reactions of Scheme I in which hydrido formyl,⁴ methyl formate,⁵ or α -hydroxymethyl⁶ derivatives are produced have been described only once. In particular, the last reaction represents the only insertion of H_2CO into a transition-metal-hydrogen bond.⁶

Here we report the reactions of formaldehyde with the two isoelectronic complexes $(\text{np}_3)\text{Ni}$ ⁷ (1) and $(\text{np}_3)\text{CoH}$ ⁷ (2) [$\text{np}_3 = \text{tris}(2\text{-}(\text{diphenylphosphine})\text{ethyl})\text{amine}$]. A comparative study of the reactivity of 1 and 2 with acetaldehyde also has been carried out. Fully synthetic details and characterization data are presented for unprecedented examples of paramagnetic formyl- and acylmetal complexes.



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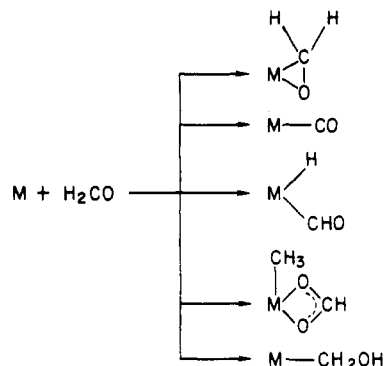
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Scheme I



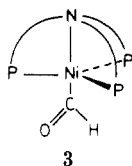
Results

Reaction of 1 with H_2CO . Two products of formula $(\text{np}_3)\text{Ni}(\text{CHO})$ (3) and $(\text{np}_3)\text{Ni}(\text{CO})$ (4) have been isolated from the reaction mixture of 1 with gaseous formaldehyde in tetrahydrofuran (eq 1). Pure compound 3 is obtained

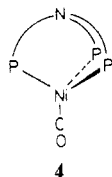
$$(\text{np}_3)\text{Ni} + \text{H}_2\text{CO} \rightarrow (\text{np}_3)\text{Ni}(\text{CHO}) + (\text{np}_3)\text{Ni}(\text{CO}) \quad (1)$$

in low yield when *n*-butyl ether is added within 1 h from the beginning of the reaction to the $1/\text{H}_2\text{CO}$ mixture. Compound 3 is a crystalline, yellow-orange solid that is rather stable in the solid state but unstable in solution even under an inert atmosphere. It is paramagnetic with a magnetic moment corresponding to one unpaired spin ($\mu_{\text{eff}} = 2.02 \mu_{\text{B}}$). The reflectance spectrum, with absorption maxima at 25 000 and 11 800 cm^{-1} , is comparable to those of trigonal-bipyramidal nickel(I) complexes of formula $(\text{np}_3)\text{NiX}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$).⁷ Similarly, the IR spectrum in the region 4000–200 cm^{-1} is superimposable on those of $(\text{np}_3)\text{NiX}$ complexes, except for bands at 2670 (w) and 1615 (s) cm^{-1} . Both the position and the intensity of these two bands are suggestive of the presence of a formyl ligand C-bonded to the metal atom.^{2a,4,8} On the basis of all of these data it is reasonable to assign to 3 a structure in which the nickel atom is coordinated in a trigonal-bipyramidal environment by the np_3 ligand and by a formyl group, as shown.

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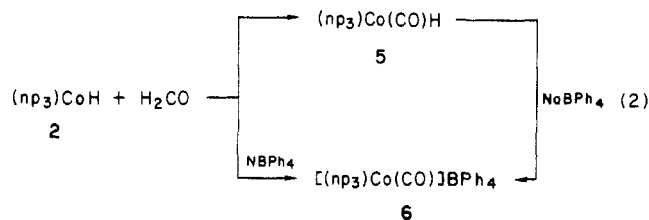


When the addition of *n*-butyl ether to the 1/H₂CO mixture in tetrahydrofuran is done after 1 h from the beginning of the reaction, the precipitation of 3 is accompanied by that of the carbonyl 4. This compound, pre-

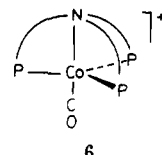
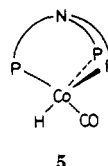


viously synthesized by a variety of alternative routes,⁹ has been characterized by an X-ray analysis.¹⁰ The nickel atom is tetrahedrally coordinated by the three phosphorus atoms of np₃ and by a CO group. The composition of the precipitate, which can be determined by means of IR spectroscopy, varies with the reaction times. Less formyl 3 and more carbonyl 4 are formed as the reaction time is lengthened. Similarly, when the formyl complex is not immediately filtered but is left standing in its reaction mixture, it slowly disappears and only yellow crystals of 4 are collected. On the basis of the above experimental results, it is not surprising that the reaction of 1 with paraformaldehyde, which requires either longer reaction times or higher temperatures than that with gaseous H₂CO, always yields a mixture of 3 and 4. As far as we know, 3 represents the first example of a paramagnetic formyl complex. The availability of paramagnetic metal formyls may provide useful information to those who are involved in the study of the metal-catalyzed reduction of CO by H₂. Key intermediates in the latter process are believed to be metalloformyl species.¹

Reaction of 2 with H₂CO. In the reactions of 2 with gaseous formaldehyde or paraformaldehyde, the presence of NaBPh₄ is important in determining the course of the reaction. The hydridometal carbonyl (np₃)Co(CO)H (5) is obtained by adding *n*-butyl alcohol to the 2/H₂CO mixture in tetrahydrofuran, whereas the addition of NaBPh₄ in *n*-butyl alcohol causes the formation of the carbonyl [(np₃)Co(CO)]BPh₄ (6) (eq 2). Both these com-

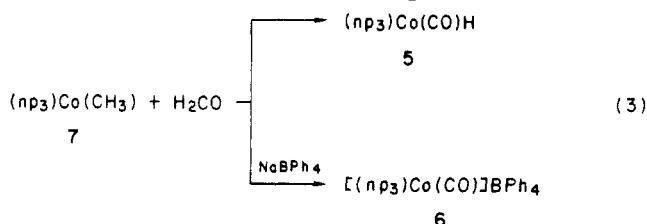


pounds have been synthesized previously by reacting CO with 2 or with [(np₃)Co]BPh₄, respectively.^{9a} We have found that the hydrido carbonyl 5 is easily converted to the carbonyl 6 by addition of NaBPh₄ to its solutions, a process which, in practice, corresponds to the displacement of the hydride ligand from 5, followed by rearrangement of np₃ and CO around the metal center. As a result, the nitrogen atom of np₃, not bound to cobalt in 5, approaches

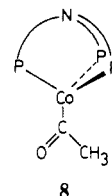


the metal and the CO ligand shifts to an apical position on the trigonal bipyramid.

In order to determine the source of the hydride ligand of 5, that is, to determine whether it comes from the parent hydride 2 or whether it is provided by formaldehyde, we have reacted H₂CO with the methyl complex (np₃)Co(CH₃) (7). Compound 7 is isoelectronic and isostructural with 2.¹ The reaction proceeds exactly in the same way as that with 2 to give the hydrido carbonyl 5 and the carbonyl 6 (eq 3). Therefore, it is reasonable to deduce that the hydride ligand in 5 comes from H₂CO.



Reaction of 1 and 2 with CH₃CHO. Compound 1 does not react at all with acetaldehyde. By contrast, 2 reacts immediately at room temperature with CH₃CHO in tetrahydrofuran to give yellow-ochre crystals of formula (np₃)Co(COCH₃) (8). Compound 8 is stable in the solid



state and insoluble in common organic solvents. It is paramagnetic with a magnetic moment corresponding to two unpaired spins ($\mu_{\text{eff}} = 3.39 \mu_B$). The electronic spectrum shows absorptions at 5700, 9600 (sh), 10500, 14300, 19200 (sh), and 25000 (sh) cm⁻¹ and is fully comparable to those of paramagnetic high-spin Co(I) complexes of formula (np₃)CoX (X = Cl, Br, I, SCN).⁷ The structure of (np₃)CoBr has been recently elucidated by X-ray methods.¹² The cobalt atom is pseudotetrahedrally coordinated to the three phosphorus atoms of np₃ and a bromine atom. The central nitrogen atom of np₃ is not coordinated to the metal in 8, as indicated by the IR spectrum, which contains a typical band at 2800 cm⁻¹, which is present whenever the apical nitrogen is free and the three phosphorus atoms are linked to the metal center.¹³ A strong band in the $\nu(\text{CO})$ stretching region at 1590 cm⁻¹ is assigned to an acetyl group C-bonded to the cobalt atom.¹⁴ On the basis of all of these data, 8 is assigned a

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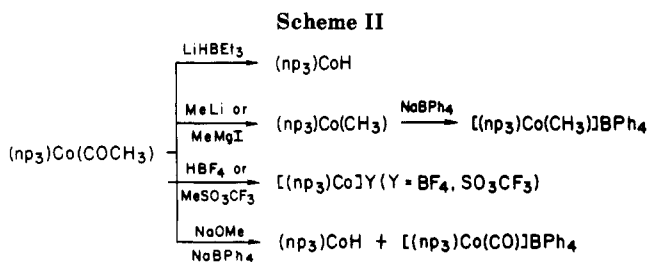
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structure where cobalt is four-coordinate with three phosphorus atoms of np_3 and an acetyl group.

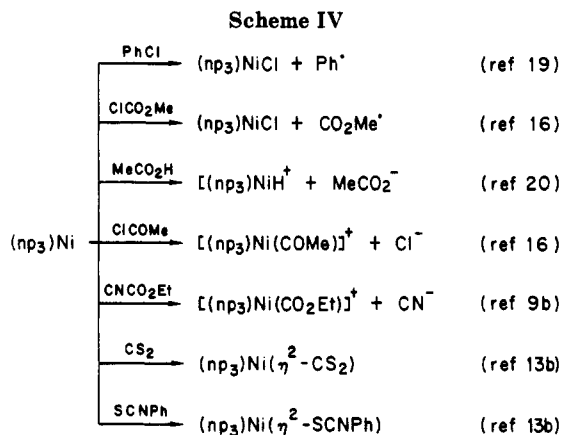
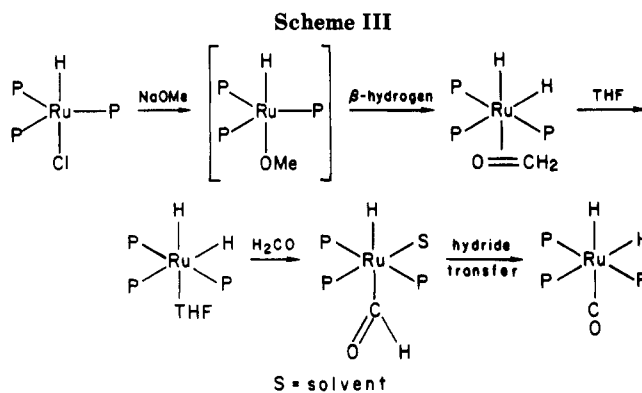
Propionaldehyde reacts similarly with **2**. The propionyl complex $(np_3)Co(COC_2H_5)$ (**9**) is obtained by allowing C_2H_5CHO to react with **2** under the same conditions employed for the CH_3CHO reaction. The physical and chemical properties of **9** are almost identical with those of **8**, and, thus, the compounds are assigned the same structure. Interestingly, neither **1** or **2** react with aromatic aldehydes such as benzaldehyde.

Reaction of 8 with LiHBEt₃, MeLi, MeMgI, NaOMe, MeOSO₂CF₃, and HBF₄. The reaction pathways involving the reactivity of **8** are conveniently summarized in Scheme II, where we have reported only the metal compounds obtained. The identification of the eventual organic coproducts is presently underway. All the complexes reported in Scheme II have been identified by comparison with pure samples, which were prepared as previously described.⁷

Nucleophiles such as H^- and CH_3^- replace the acetyl ligand from **8** to give the corresponding Co(I) complexes, whereas electrophiles such as H^+ and CH_3^+ remove the acetyl group restoring the $[(np_3)Co]^+$ moiety. The stabilization of the Co(II) derivative by treatment of the Co(I) complex with BPh_4^- anions has been observed for other $(np_3)CoX$ complexes ($X = NO$,¹⁵ CN ,¹⁶ $-CR=CH_2$).¹⁶

It would be interesting to know what happens to the acetyl group. In fact, organotransition-metal acyl complexes have found extensive use in organic syntheses both in catalytic and in stoichiometric reactions.¹⁷ In particular, a variety of carbonyl compounds such as aldehydes, ketones, acids, esters, amides, etc. have been obtained via decomplexation of metal acyls.

The only reaction of Scheme II which presents particular problems is that with NaOMe. By treatment of **8** in tetrahydrofuran with NaOMe in methanol, a red-brown solution is produced, from which a few crystals of **2** are precipitated by addition of butanol. Red crystals of the carbonyl **6** are, then, obtained by adding NaBPh₄ to the mother liquor. Generally, the amount of the carbonyl is at least 10 times greater than that of the hydride. It is not easy to rationalize this reaction. The facility by which nucleophiles can displace the acetyl ligand from **8** suggests the intermediacy of a methoxo complex and an overall reaction mechanism similar to that reported for the formation of $RuH_2(CO)(PPh_3)_3$ from $RuHCl(PPh_3)_3$ and NaOMe^{3a} (Scheme III). A methoxo complex also has been proposed as key intermediate in the formation of the η^2 -formaldehyde complex $W(PMe_3)_4(\eta^2-CH_2O)H_2$ from $W(PMe_3)_4(\eta^2-CH_2PMe_2)H$ and MeOH.¹⁸ The presence at a certain stage of the reaction of both H_2CO and the hydride **2** in the reaction mixture might explain the formation



of the final carbonyl **6** as in the direct reaction of **2** with H_2CO (see reaction 2). Neither the hydride **2** nor the carbonyl **6** could be obtained by reacting **8** with NaOEt.

Discussion

Understanding the reactions of H_2CO and CH_3CHO with **1** and **2** would be easier if the chemistry of the latter complexes was known, and the following experimental and theoretical results provide valuable clues.

(a) Compound **1** has a strong tendency to undergo oxidative-addition reactions with either an overall one-electron change or an overall two-electron change. As a result, d^9 paramagnetic^{16,19} or d^8 diamagnetic^{9b,13b,16,20} five-coordinate derivatives are formed. Some typical examples are given in Scheme IV.

Most of the compounds in Scheme IV have trigonal-bipyramidal structures with np_3 acting as a tetradentate ligand except for the bottom two complexes, where np_3 uses only the phosphorus atoms to bind to the metal, while the nitrogen atom is free. The coordination geometry is distorted square pyramidal.

It can be deduced from Scheme IV that the type of oxidative addition reaction that **1** undergoes is strictly dependent upon the nature of the oxidizing "addenda". In particular, small variations in reagents ($ClCO_2Me$ vs. $NCCO_2Et$ or $ClCOMe$) cause great differences in the reaction paths. The occurrence of a radical mechanism has been unequivocally established for the reaction of **1** with organic halides, which, in the case of chlorobenzene, yields as coproducts benzene, biphenyl, and *o*-, *m*-, and *p*-chlorobenzene.¹⁹

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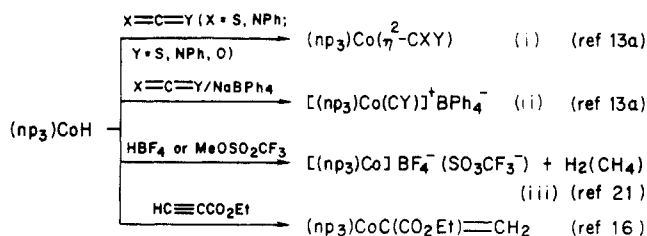
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Scheme V

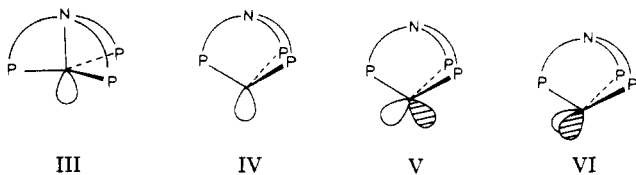


(b) If the chemistry of **1** is governed by its basicity, that of **2** is ruled by the multivarious nature of the hydrogen atom linked to cobalt. There is evidence that, depending on the type of reaction involved, **2** behaves as a donor of H, H⁺, and H⁻ atoms.²¹ Significant examples illustrating the chemistry of **2** are reported in Scheme V. Compound **2** reacts with heteroallene molecules of formula X=C=Y (X, Y = O, S, NPh) to give the corresponding paramagnetic η^2 -CXY complexes. In all of these compounds the nitrogen atom of np_3 is not coordinated to the metal center.^{13a} When the same reactions are carried out in the presence of NaBPh₄, fragmentation of the heteroallene molecules occurs and the trigonal-bipyramidal Co(I) complexes with CS, CO, and CNPh are formed.^{13a} It has been suggested that reactions of type i shown in Scheme V involve the homolytic cleavage of the cobalt-hydrogen bond. Conversely, **2** should behave as a proton donor to explain the fragmentation reactions of type ii.^{21,22} Finally, **2** releases hydride in reactions with protic acids,²¹ alkylating agents,²¹ or activated alkynes¹⁶ (type iii). In any case, the addition of a reagent to **2** results in the displacement of the hydrogen atom from the metal except when the reagent is CO. In this case, it has been possible to isolate a complex containing both the hydrogen atom and CO, $(np_3)Co(CO)H$ (**5**).

(c) The chemistry of systems of the type $(np_3)Ni$ and $(np_3)MX$ ($M = Co, Rh, Ni$; X = monodentate ligand) have also been investigated recently from a theoretical point of view.^{12,20b,23} Crystallographic evidence shows that the interconversion between a trigonal pyramid (I) and an hemoctahedral fragment (II), where nitrogen is not metal



bound, is allowed by the flexibility of the np_3 ligand. MO calculations show that for d^{10} metals the interconversion is symmetry allowed and requires an activation energy of a few kilocalories per mole. Obviously, on going from I to II, the frontier orbitals at the metal undergo a dramatic rearrangement. In practice, I has a low-energy σ -hybrid (III), whereas II has a high-lying σ -hybrid (IV), and a set of degenerate π -hybrids (V and VI). As a result, fragment

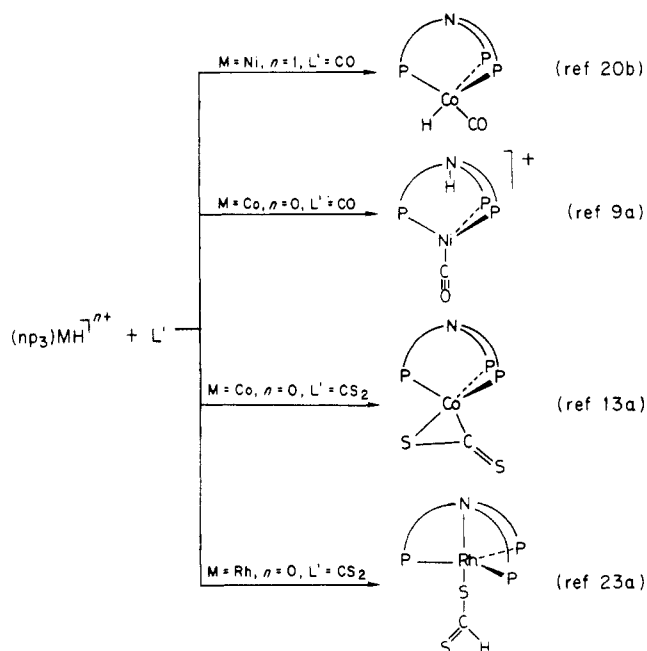


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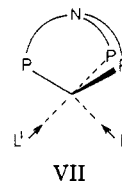
(22) Bianchini, C.; Meli, A. *J. Am. Chem. Soc.* **1984**, *106*, 2698.

(23) (a) Bianchini, C.; Masi, D.; Mealli, C.; Meli, A.; Sabat, M. *Organometallics* **1985**, *4*, 1014. (b) Mealli, C.; Sacconi, L. *Inorg. Chem.* **1982**, *21*, 2870.

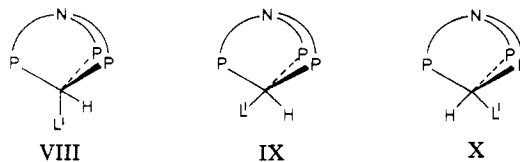
Scheme VI



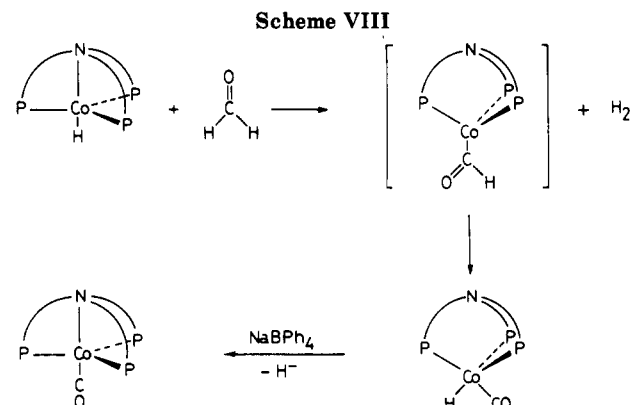
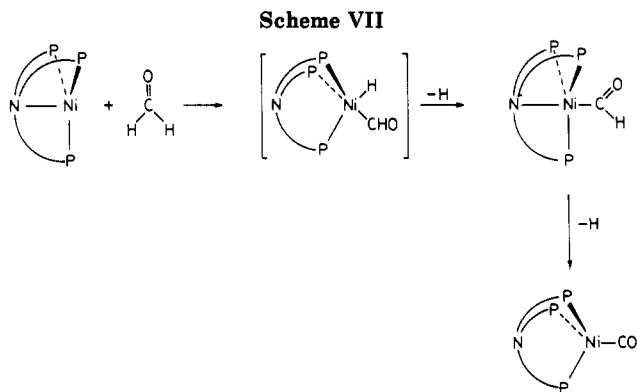
I combines best with one ligand, whereas II, in principle, can take up to three ligands. It is noteworthy, however, that stable adducts of $(np_3)M$ with more than one coligand are rarely observed. The apical amine group of np_3 usually competes for coordination with other coligands, as schematically shown in VII for the case of a bis(ligand) adduct.



When the nitrogen atom reenters the coordination sphere, the $(np_3)M$ fragment resumes shape I and the expulsion of either L or L' ensues. The surviving ligand shifts over the threefold axis, and the trigonal-bipyramidal $(np_3)ML$ (or L') species is formed. This process is reversible; as a suitable ligand L' approaches, the $(np_3)ML$ complex may be activated in the sense that the M-N bond elongates and L moves with respect to the threefold axis of the molecule to accommodate the incoming ligand. The relative disposition of L and L' seems to be important in determining the evolution of the intermediate, with two coligands, to the final product. In particular, when L = H, it has been calculated that an accumulation of negative charge on the hydrogen atom takes place on going from models VIII-X.^{23a} Which factors determine the type of $(np_3)MH(L')$



adduct formed is not yet understood in detail. Surely, the nature of the metal and the entering coligand are of critical importance in determining the geometry of the intermediate, and, hence, the nature of the hydrogen ligand, as attested by the chemical evidence reported in Scheme VI. In the first reaction of Scheme VI, the hydrogen ligand migrates as a proton from the metal to the amine group of np_3 . By contrast, hydrogen has an hydridic nature in



the hydrido carbonyl **5** reported in the second reaction, as demonstrated by the facile expulsion of H^- from **5** to give the corresponding carbonyl cation $[(\text{np}_3)\text{Co}(\text{CO})]^+$. Finally, the reactions of **2** and the isomorphous $(\text{np}_3)\text{RhH}$ complex²² with CS_2 show how the metal may influence the nature of the hydrogen ligand. The hydrogen atom migrates as an hydride in the rhodium reaction, whereas the formation of the cobalt $\eta^2\text{-CS}_2$ adduct is easily rationalized by assuming that a hydrogen atom is expelled from **2**.

The points above should be properly evaluated when discussing the reactivity of **1** and **2** toward H_2CO and CH_3CHO .

The formation of a formyl complex containing a d^9 metal is suggestive of a one-electron oxidative addition of formaldehyde to the d^{10} nickel complex **1**. It is difficult to say through which mechanism the reaction may proceed in the absence of detectable intermediates and kinetic studies. However, by analogy with the reactions of **1** with organic halides or with methyl chloroformate, it is very reasonable to suggest a radical mechanism as shown in Scheme VII. Similarly, the decomposition of the formyl **3** to the carbonyl **4** may have radical character. It has been reported recently, in fact, that neutral formyl complexes can decompose by a pathway initiated by cleavage of the carbon-to-hydrogen bond of the formyl group by miscellaneous radicals (in our case H atoms).²⁴

Now consider the reaction of **2** with H_2CO . Finally, this is a classic decarbonylation reaction of an aldehyde by a metal complex, a process which is believed to proceed through the oxidative addition of the C-H bond of aldehydes to the metal to give hydridometal acyl (or formyl) intermediates.²⁵ Actually, we are not able to draw conclusions about the initial interaction of the H_2CO group with the hydride **2**. In the light of the results reported throughout this paper, however, the formation of the Co(I) formyl $(\text{np}_3)\text{Co}(\text{CHO})$ at a certain stage of the reaction is very likely. This could explain the isolation of the final hydrido carbonyl **5** (Scheme VIII). The intramolecular migration step $\text{M}(\text{CHO}) \rightarrow \text{M}(\text{CO})\text{H}$ is, in fact, well established.^{1,26} Support for the pathway shown in Scheme VIII is provided by the results of both the reaction of the methyl derivative **7** with H_2CO and the reaction of **2** with CH_3CHO . In particular, the former reaction indicates that the hydrogen ligand of **5** originally belongs to H_2CO , whereas the latter, which yields the stable four-coordinate

Co(I) acetyl **8**, makes reasonable both the occurrence and the structure of the formyl intermediate in Scheme VIII.

Experimental Section

Literature procedures were allowed to prepare **1**, **2**, and **7**. Reagent grade chemicals were used in the preparation of the complexes. Tetrahydrofuran (THF) was purified by distillation over LiAlH_4 just before use. *n*-Butyl ether and *n*-pentane were distilled over sodium and stored under nitrogen. All operations were routinely performed under nitrogen by using deoxygenated solvents. The solid complexes were collected on a sintered-glass frit and dried in a stream of nitrogen. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer using samples milled in Nujol between CsI plates. Ultraviolet-visible spectra were recorded on a Beckman DK-2A spectrophotometer. Magnetic susceptibilities of solid samples were measured on a Faraday balance. GLC measurements were made on a Carlo Erba frac-tovap, Model B.

Reaction of $(\text{np}_3)\text{Ni}$ (1**) with H_2CO .** (A) Formaldehyde prepared by heating paraformaldehyde (0.3 g) was carried in a slow stream of nitrogen into a magnetically stirred solution of **1** (0.36 g, 0.5 mmol) in THF (50 mL). The resulting mixture was stirred for 40 min, filtered to eliminate the excess of paraformaldehyde, and concentrated under vacuum to ca. 20 mL. By addition of *n*-butyl ether (30 mL) yellow orange crystals of $(\text{np}_3)\text{Ni}(\text{CHO})$ (**3**) began to separate, which were immediately filtered and washed with a 1:2 mixture of THF/*n*-butyl ether and *n*-pentane. Anal. Calcd for $\text{C}_{43}\text{H}_{43}\text{NNiOP}_3$: C, 69.65; H, 5.84; N, 1.88; Ni, 7.91. Found: C, 69.37; H, 5.76; N, 1.91; Ni, 7.83. When the reaction mixture was stirred for times >1 h, the precipitation of **3** was accompanied by that of the carbonyl $(\text{np}_3)\text{Ni}(\text{CO})$ (**4**). The longer the reaction times were, the more carbonyl was collected. Pure compound **4** in 70% yield was obtained by reacting **1** and H_2CO for 10 h. (B) A mixture of **1** (0.35 g, 0.5 mmol) and paraformaldehyde (0.3 g) in THF (60 mL) was stirred at room temperature for 3 days during which time the red solution turned orange. Filtration followed by concentration under vacuum and addition of *n*-butyl ether (30 mL) gave a yellow-orange crystalline solid consisting of a mixture of **3** and **4**. (C) Paraformaldehyde (0.3 g) and **1** (0.35 g, 0.5 mmol) in THF (50 mL) were heated under reflux for 1 h. Filtration, concentration of the resulting solution, and addition of *n*-butyl ether (30 mL) gave a mixture of **3** and **4**. Pure compound **4** was obtained by refluxing the reaction mixture for 3 h.

Reaction of $(\text{np}_3)\text{CoH}$ (2**) with H_2CO .** Gaseous formaldehyde from paraformaldehyde (0.1 g), was bubbled into a magnetically stirred solution of **2** (0.36 g, 0.5 mmol) in THF (20 mL). There was an immediate color change from orange to yellow-brown. Hydrogen evolution was observed by chromatographic methods. After 15 min the excess of paraformaldehyde was eliminated by filtration. Butanol (20 mL) was added, and the solution was concentrated to give yellow crystals of $(\text{np}_3)\text{Co}(\text{CO})\text{H}$ (**5**) in 80% yield. Alternatively, when NaBPh_4 (0.21 g, 0.6 mmol) was added along with butanol to the reaction mixture, the solution turned dark red within a few minutes and red-orange crystals of $[(\text{np}_3)\text{Co}(\text{CO})]\text{BPh}_4$ (**6**) were formed; yield 80%. Both compounds **5** and **6** were also obtained in the same yields by reacting **2** with paraformaldehyde in THF either at room temperature for 2 h or at reflux temperature for 30 min.

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Reaction of $(\text{np}_3)\text{Co}(\text{CH}_3)$ (7) with H_2CO . A mixture of 7 (0.37 g, 0.5 mmol) and paraformaldehyde (0.1 g) in THF (20 mL) was heated under reflux for 2 h to give a yellow brown solution. Addition of butanol (30 mL) gave yellow crystals of 5 in 60% yield. The red carbonyl 6 also was obtained by adding NaBPh_4 .

Reaction of $(\text{np}_3)\text{CoH}$ with CH_3CHO . Acetaldehyde (3 mL) was added to solution of 2 (0.36 g, 0.5 mmol) in THF (50 mL). The color of the solution changed rapidly from orange to yellow-brown and yellow-ochre crystals of $(\text{np}_3)\text{Co}(\text{COCH}_3)$ (8) began to separate after 10 min. After the mixture was left standing overnight at room temperature, the precipitation of the crystals was complete. They were collected and washed with THF and *n*-pentane; yield 70%. The same reaction can be carried out in benzene or DMF. Anal. Calcd for $\text{C}_{44}\text{H}_{46}\text{CoNOP}_3$: C, 69.93; H, 6.00; Co, 7.79; N, 1.85. Found: C, 69.67; H, 5.93; Co, 7.78; N, 1.81.

Reaction of $(\text{np}_3)\text{CoH}$ with $\text{C}_2\text{H}_5\text{CHO}$. Yellow crystals of $(\text{np}_3)\text{Co}(\text{COC}_2\text{H}_5)$ were obtained in 70% yield from 2 and propionaldehyde by a procedure analogous to the one above. Anal. Calcd for $\text{C}_{45}\text{H}_{47}\text{CoNOP}_3$: C, 70.21; H, 6.15; Co, 7.65; N, 1.82. Found: C, 70.09; H, 6.06; Co, 7.59; N, 1.85.

Reaction of $(\text{np}_3)\text{Co}(\text{COCH}_3)$ (18) with LiHBET_3 . A THF (20 mL) suspension of 8 (0.38 g, 0.5 mmol) was treated with 0.75 mL of LiHBET_3 (1 M in THF) at 0 °C. A fast reaction took place producing a red-orange solution. On addition of butanol (30 mL) orange crystals of 2 were formed, which were filtered and washed with ethanol and petroleum ether; yield 60%.

Reaction of $(\text{np}_3)\text{Co}(\text{COCH}_3)$ with MeLi or MeMgI . To a suspension of 8 (0.38 g, 0.5 mmol) in THF (20 mL) was added a 5% solution of MeLi (or MeMgI) in diethyl ether (0.4 mL) at

room temperature which caused the solid to dissolve to give an orange solution. Addition of butanol (30 mL) gave red crystals of 7; yield 60%. Alternatively, when NaBPh_4 (0.34 g, 1 mmol) in butanol (20 mL) was added to the reaction mixture, red crystals of $(\text{np}_3)\text{Co}(\text{CH}_3)\text{BPh}_4$ were obtained in 60% yield.

Reaction of $(\text{np}_3)\text{Co}(\text{COCH}_3)$ with NaOMe . A 1 M solution of sodium methoxide in methanol (0.6 mL) was added to a suspension of 8 (0.38 g, 0.5 mmol) in THF (40 mL), and the resulting mixture was stirred magnetically for 2 days. During this time the solid dissolved to give a red solution. On addition of butanol (30 mL) red crystals of 2 were obtained in 5% yield. Addition of NaBPh_4 (0.34 g, 1 mmol) to the mother liquor led to the precipitation of red crystals of $(\text{np}_3)\text{Co}(\text{CO})\text{BPh}_4$; yield 50%.

Reaction of $(\text{np}_3)\text{Co}(\text{COCH}_3)$ with HBF_4 or $\text{MeOSO}_2\text{CF}_3$. A THF (30 mL) suspension of 8 (0.38 g, 0.5 mmol) was reacted with a slight excess of HBF_4 /diethyl ether (or $\text{MeOSO}_2\text{CF}_3$) at 0 °C. Within a few minutes a yellow-green solution was produced from which green crystals of $(\text{np}_3)\text{Co}\text{BF}_4$ (or SO_3CF_3) precipitated on standing; yield 90%.

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Registry No. 1, 97135-31-4; 2, 97135-32-5; 3, 97135-33-6; 4, 88440-32-8; 5, 97135-35-8; 6, 97135-37-0; 7, 97135-38-1; 8, 97149-88-7; $(\text{np}_3)\text{Co}(\text{COC}_2\text{H}_5)$, 97135-39-2; $(\text{np}_3)\text{Co}(\text{CH}_3)\text{BPh}_4$, 97135-41-6; $(\text{np}_3)\text{Co}\text{BF}_4$, 97135-43-8; $(\text{np}_3)\text{Co}\text{SO}_3\text{CF}_3$, 97149-89-8; formaldehyde, 50-00-0; acetaldehyde, 75-07-0; propionaldehyde, 123-38-6.

Carbonylation of Phenylplatinum(II) Complexes Containing Bidentate Ligands

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A series of complexes of the type $[\text{PtClPh}(\text{P}^{\wedge}\text{Y})]$ ($\text{P}^{\wedge}\text{Y} = 1,2\text{-bis}(\text{diphenylphosphino})\text{ethane}$ (dppe), 1-(diphenylphosphino)-2-(diphenylarsino)ethane (appe), 1,3-bis(diphenylphosphino)propane (dppp), 1-(diphenylphosphino)-2-(methylthio)ethane (PC_2S), or 1-(diphenylphosphino)-2-(dimethylamino)ethane (PC_2N)) has been prepared and the carbonylation reactions of these complexes investigated. The corresponding benzoyl complexes have been generated by an alternative route. No reaction of $[\text{PtClPh}(\text{P}^{\wedge}\text{Y})]$ with CO takes place when $\text{P}^{\wedge}\text{Y} = \text{dppe}$ or appe , but carbonylation proceeds smoothly, albeit slowly, when $\text{P}^{\wedge}\text{Y} = \text{dppp}$, PC_2S , or PC_2N . The reaction is most rapid for the dppp complex. These results are rationalized in terms of both dissociative and nondissociative reaction pathways.

Introduction

The carbonylation of organoplatinum(II) complexes of the type $\text{trans-}[\text{PtXRL}_2]$ (X = halide; R = alkyl or aryl; L = tertiary phosphine) has been extensively studied,¹ where the acyl or aryl products obtained are also of *trans* geometry. The reaction has been shown^{2,3} to proceed by two competing pathways; one involves organic group migration from the five-coordinate adduct $[\text{PtXR}(\text{CO})\text{L}_2]$, whereas the second occurs by dissociation of L and organic group migration within the four-coordinate complex $[\text{PtXR}(\text{CO})\text{L}]$ thus formed. The dissociative route is dominant for L = triarylphosphine, but phosphine disso-

ciation does not occur during the carbonylation of *trans-}[\text{PtClPh}(\text{PMePh}_2)_2].³*

The involvement of *cis* complexes in the carbonylation scheme has been suggested,¹ but the ready isomerization of complexes of the type *cis-}[\text{PtXRL}_2] renders impractical the study of their reactions with carbon monoxide. We have previously noted the lack of reactivity of $[\text{PtClPh}(\text{dppe})]$ and $[\text{PtClPh}(\text{appe})]$ (dppe = 1,2-bis(diphenylphosphino)ethane; appe = 1-(diphenylphosphino)-2-(diphenylarsino)ethane) toward carbon monoxide,⁴ although their reactions were only monitored in solution by ³¹P{¹H} NMR spectroscopy. We report here the preparation of a series of complexes of the type $[\text{PtClPh}(\text{P}^{\wedge}\text{Y})]$ ($\text{P}^{\wedge}\text{Y} = \text{dppe}$, appe , dppp , $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SMe}$, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_2$),*

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