influence of the diaquo species, leading to an arrangement that actually stabilizes the blue component.

Summary

The versatility of unsubstituted uracil as a ligand of platinum has been demonstrated. $(NH_3)_3Pt^{II}$, $enPt^{II}$, and *cis*-$(NH_3)_2Pt^{II}$ form a variety of complexes which contain uracil in its neutral, monoanionic, and dianionic form bonded through N-1, N-3 in a monodentate bridging fashion or through different N,O atoms in a bidentate fashion. In aqueous solution at a pH <7, a series of different modes of coordination coexist. There is an interconversion of the various species under the influence of coordinatively "unsaturated" platinum species such as $(NH_3)_3Pt(H_2O)^{2+}$, $enPt(H_2O)_2^{2+}$, $(NH_3)_2Pt(H_2O)_2^{2+}$, $enPt(HU)H_2O^+$, or $(NH_3)_2Pt(HU)H_2O^+$, as demonstrated most clearly with the $(NH_3)_3Pt^{II}$ system. The interconversion in all cases seems to proceed via uracil-bridged species. The assignment of the donor atoms in these bridged species represents a problem. Only in one case, with compound A in the $enPt^{II}$ system, an assignment (N-1, O-2) was possible based on rather indirect evidence, whereas in all other cases no definitive conclusions have been possible. It is felt that only X-ray crystallography eventually can give an answer to the question concerning the different ways of bridging and go beyond a mere classification derived at by vibrational and NMR spectroscopy. The coexistence of different species in solution and the apparent easy interconversion seems to indicate very similar thermodynamic stabilities of the various species.

With respect to some of the characteristics of N-1 and N-3 tautomer complexes of uracil, the described results verify earlier findings[12,35] that N-3 complexes are more readily protonated and more easily decomposed by acid than the corresponding N-1 complexes. Interestingly, N-3 complexation of the uracil monoanion is favored over N-1 complexation in slightly acidic medium, whereas the situation is reversed in alkaline medium. N-1 and N-3 tautomer complexes (or bridged complexes involving these donor atoms) also exhibit different tendencies to undergo isotopic exchange at C-5 in D_2O: a rapid $^2D/^1H$ exchange takes place with complexes containing N-1-bound platinum in acidic medium, with no exchange in N-3 complexes under comparable conditions.

As to the usefulness of the techniques applied in this study, ^1H NMR and Raman spectroscopy, the following conclusions can be drawn.

(1) The study of Raman-active vibrations of the heterocyclic ring in principle represents a useful tool for the differentiation of various types of metal binding. Raman spectroscopy is limited in its usefulness by the occasional strong overlap of corresponding modes in mixtures containing more than two or three different types of complexes and by the dark colors of some of the mixtures. A differentiation of 1:1 and 2:1 complexes with identical donor atoms cannot be achieved. On the other hand, Raman spectroscopy is able to distinguish complexes with their ligands being in a pH-dependent equilibrium.

(2) ^1H NMR spectroscopy appears to be a more stable technique for this type of studies on tautomer complexes. However, its applicability is restricted to kinetically inert species. With kinetically labile systems, information from NMR spectra is limited. The same applied to paramagnetic complexes (e.g., platinum uracil "blues" and "tans").

Acknowledgment. The author wishes to thank the Deutsche Forschungsgemeinschaft, DFG, and the Technische Universität München for financial support and R. Pfab for many discussions.

Registry No. *cis*-$(NH_3)_2Pt(HU\text{-}N1)Cl$, 79084-56-3; $[(NH_3)_3Pt(HU\text{-}N1)]Cl$, 79084-57-4; $[(NH_3)_3Pt(HU\text{-}N1)]NO_3$, 68264-66-4; $(NH_3)_3Pt(U\text{-}N1)$, 79084-58-5; $(NH_3)_3Pt(U\text{-}N3)$, 79084-59-6; $enPt(HU\text{-}N1)Cl$, 72016-76-3; $enPt(HU\text{-}N1)_2$, 79084-60-9; $[enPt(HU)]_2(NO_3)_2$, 79084-62-1; *cis*-$(NH_3)_2Pt(HU\text{-}N1)_2$, 79084-63-2; $Na_2[(NH_3)_2Pt(U\text{-}N1)_2]$, 79084-64-3; *cis*-$[(NH_3)_2Pt(HU\text{-}N1)H_2O]NO_3$, 79084-66-5; K(HU), 79069-71-9; Na(HU), 42563-71-3; H_2U, 66-22-8; $enPt(HU\text{-}N1)H_2O^+$, 79084-67-6; $enPt(HU\text{-}N3)H_2O^+$, 79084-68-7; $(NH_3)_2Pt(HU\text{-}N3)H_2O^+$, 79084-69-8; $[(NH_3)_3Pt(HU\text{-}N3)]NO_3$, 68265-07-6; *cis*-$[(NH_3)_2Pt(DMF)Cl]NO_3$, 79084-71-2; *cis*-$[(NH_3)_2Pt(DMF)_2](NO_2)_2$, 79084-73-4; $[(NH_3)_3Pt(H_2O)](NO_3)_2$, 79084-74-5; *cis*-$[(NH_3)_2Pt(H_2O)_2]^{2+}$, 20115-64-4; $enPtCl_2$, 14096-51-6; *cis*-$(NH_3)_2PtCl_2$, 15663-27-1.

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Effects of Steric Requirement and Ligand Basicity in Phosphine Substitution Reactions of Dicobalt Octacarbonyl

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The kinetics of the substitution of $Co_2(CO)_8$ by $P(i\text{-}Pr)_3$, $P(t\text{-}Bu)_3$, and $P(CH_2CH_2CN)_3$ in CH_2Cl_2 have been studied. The rate law for reaction with $P(t\text{-}Bu)_3$ and $P(CH_2CH_2CN)_3$ at 20 °C is first order in $CO_2(CO)_8$, with no dependence on base concentration. The first-order rate constants are 1.7×10^{-2} and 1.3×10^{-2} s^{-1}, respectively. Addition of CO results in a decrease in reaction rate. A mechanism involving a rate-determining CO dissociation is proposed. Reaction with $P(i\text{-}Pr)_3$ is complex; products formed are $Co(CO)_3[P(i\text{-}Pr)_3]_2{}^+Co(CO)_4{}^-$ and $Co_2(CO)_6[P(i\text{-}Pr)_3]_2$. Observed order in carbonyl is 1.5 at 0 °C and 1.3 at 25 °C. Nonintegral order in base is also observed. A radical chain mechanism analogous to that previously proposed for reaction with $P(n\text{-}Bu)_3$ accounts for the kinetic behavior. These results suggest that reaction with bases of low nucleophilicity or large steric requirement proceeds via a rate-determining CO dissociation. With more nucleophilic bases of small or intermediate steric requirement, a radical chain mechanism is observed. The manner in which the steric requirement of the base can affect the radical chain mechanism is discussed.

The reactions of dicobalt octacarbonyl with group 5 bases give rise to several different products. With phosphines, the usual initial product is $[Co(CO)_3L_2][Co(CO)_4]$.[1-7] This salt can be converted to the dinuclear species, $Co_2(CO)_6L_2$, by heating in refluxing benzene.[8-11] The product obtained with

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phosphites may be either the salt, $[Co(CO)_2L_3][Co(CO)_4]$, or the substituted dinuclear compound $Co_2(CO)_6L_2$, depending upon reaction conditions.[12,13] The phosphite salt is not smoothly converted to the dinuclear compound; instead a Michaelis–Arbuzov rearrangement occurs to give the acyl complex $RCOCo(CO)_2L_2$.[14] With arsines, $Co_2(CO)_7L$ is first formed and then $Co_2(CO)_6L_2$;[15,16] no disproportionation products are obtained.

In a previous paper,[17] we have reported a kinetic study of the substitution reaction of $Co_2(CO)_8$ with $P(n\text{-}Bu)_3$, PPh_3, and $AsPh_3$. In that work two distinct reaction pathways for substitution were observed. The phosphines react by a radical chain mechanism in which metal–metal bond homolysis is induced by base attack at the metal center. This base-induced metal–metal bond homolysis initiates the radical chain process. In contrast, we have proposed that reaction with $AsPh_3$ occurs by an initial rate-determining CO dissociation to give the $Co_2(CO)_7$ moiety, which then rapidly adds arsine. This CO dissociation mechanism has previously been invoked in reaction of $Co_2(CO)_8$ with acetylenes,[18,19] hydrogen,[20] and isotopically labeled CO.[17,21] Failure of $AsPh_3$ to give rise to the radical mechanism was thought to be due to the lower basicity of the arsine relative to the phosphines. In an effort to determine what factors are important in determining which of these two pathways for substitution will dominate, we have investigated how the reaction course is influenced by the nucleophilicity and steric requirement of phosphine bases.

Experimental Section

Materials. Nitrogen (Linde high purity) was purified of traces of oxygen by passing through an activated manganese oxalate column.[22] Triisopropylphosphine ($P(i\text{-}Pr)_3$) and tri-*tert*-butylphosphine ($P(t\text{-}Bu)_3$) (Strem Chemical) were distilled from CaH_2 under reduced pressure of nitrogen. Tris(2-cyanoethyl)phosphine (Strem Chemical) was twice recrystallized from ethanol. Dichloromethane (MCB) was degassed by bubbling nitrogen through the solvent for approximately 15 min followed by distillation from P_2O_5 under purified nitrogen. Dicobalt octacarbonyl was sublimed under reduced pressure at 37 °C.

Instrumentation. All measurements were taken on a Beckman 4240 infrared spectrophotometer which was interfaced to a cassette tape deck. Data recorded on cassette tape as absorbance vs. time were read into a PDP-11 computer for numerical analysis. Temperature inside the cell compartment was maintained to within ±0.2 °C by a YSI Model 74 Thermistemp temperature controller.

Reaction Products. Reaction with $P(t\text{-}Bu)_3$ and $P(CH_2CH_2CN)_3$ gives a mixture of the mono- and disubstituted dinuclear products $Co_2(CO)_7L$ and $Co_2(CO)_6L_2$. Reaction with $P(i\text{-}Pr)_3$ results in formation of the disproportionation product $[Co(CO)_3L_2][Co(CO)_4]$ as the major product; trace amounts of the disubstituted dinuclear species are also present. The products were identified by their IR spectra and, and in some cases, elemental analyses. The observed IR spectra in the region of the CO stretching modes in CH_2Cl_2 were as follows: $Co_2(CO)_7P(t\text{-}Bu)_3$, 2080 (m), 2022 (m), 2000 (vs), 1955 (w) cm^{-1}; $Co_2(CO)_6[P(t\text{-}Bu)_3]_2$, 1970 (m, sh), 1950 (vs) cm^{-1}; $Co_2(CO)_7P(CH_2CH_2CN)_3$, 1975 (m, sh), 1968 (m) cm^{-1}; $Co(CO)_3[P(i\text{-}Pr)_3]_2Co(CO)_4$, 1990 (s), 1887 (vs) cm^{-1}; $Co_2(CO)_6[P(i\text{-}Pr)_3]_2$, 1963 (m, sh), 1943 (vs) cm^{-1}.

Kinetics. All experiments were carried out under pseudo-first-order conditions of base. Dicobalt octacarbonyl concentrations in range $(1.0\text{–}1.5) \times 10^{-3}$ M were used with base concentrations in the range $(2.0\text{–}9.0) \times 10^{-2}$ M. Reaction progress was followed by monitoring absorbance of the 2042-cm^{-1} band of $Co_2(CO)_8$. Solutions were prepared in an inert-atmosphere glovebox maintained with oxygen and water content at less than 5 ppm each by methods previously described.[22] Solutions were placed in amber bottles that were fitted with tight-fitting rubber septa. Visible light was excluded during the course of the reaction by means of a germanium filter placed in the IR beam. Care was taken to exclude oxygen by maintaining a positive

Table I. Observed Pseudo-First-Order Rate Constants for $Co_2(CO)_8$[a] Reaction with Various Concentrations of $P(t\text{-}Bu)_3$ in CH_2Cl_2 at 25 °C

$10^2[P(t\text{-}Bu)_3]$, M	10^2k_{obsd}, s^{-1}
1.00	2.05 (±0.15)[b]
1.00[c]	1.55 (±0.02)
1.98	1.79 (±0.05)
2.57	1.69 (±0.16)
2.97	1.68 (±0.01)
2.97[d]	1.63 (±0.02)

[a] $Co_2(CO)_8$ concentration of about 10^{-3} M. [b] Numbers in parentheses are standard deviations based on several kinetics runs made at each base concentration. [c] CO added to both solutions before reaction. [d] Air added to base solution before reaction.

Table II. Observed Pseudo-First-Order Rate Constants for $Co_2(CO)_8$[a] Reaction with Various Concentrations of $P(CH_2CH_2CN)_3$ in CH_2Cl_2 at 25 °C

$10^2[P(CH_2CH_2CN)_3]$, M	10^2k_{obsd}, s^{-1}
1.04	1.32 (±0.06)[b]
1.04[c]	1.21 (±0.04)
3.01	1.29 (±0.05)
4.97	1.21 (±0.05)

[a] $Co_2(CO)_8$ concentration of about 10^{-3} M. [b] Numbers in parentheses are standard deviations. [c] CO added to both solutions before reaction.

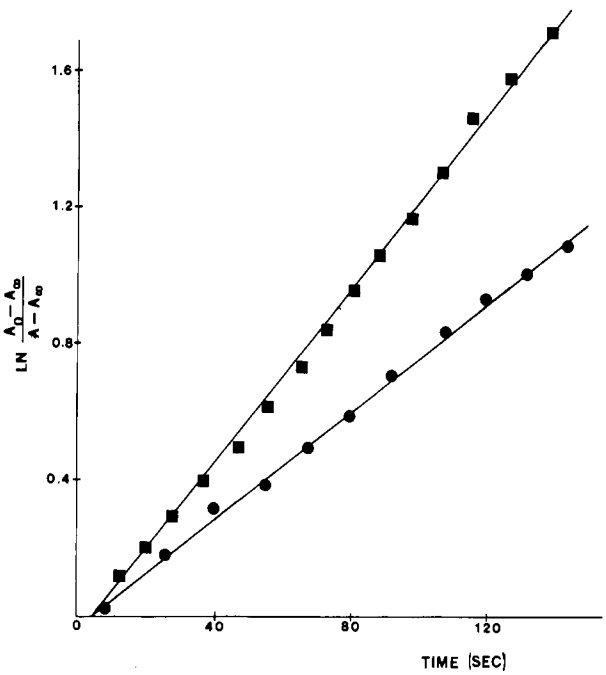

Figure 1. Pseudo-first-order plot for reaction of $Co_2(CO)_8$ (10^{-3} M) with $P(t\text{-}Bu)_3$ (10^{-2} M) in CH_2Cl_2 at 25 °C: ■, absence of CO; ●, presence of CO.

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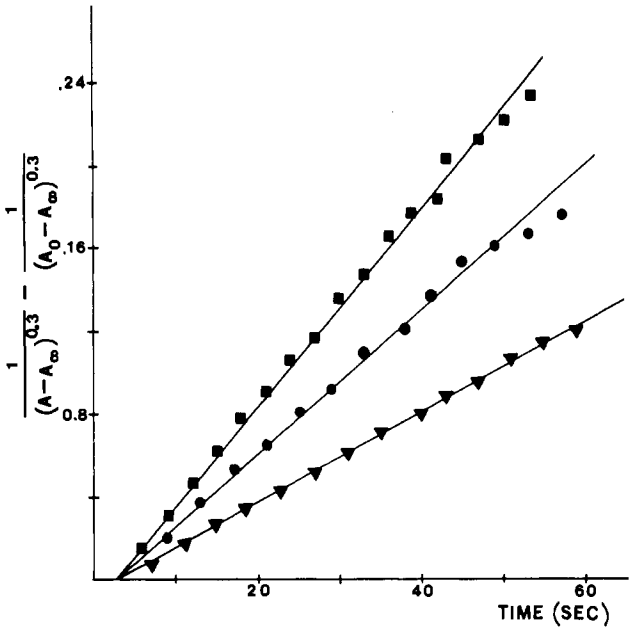

Figure 2. Pseudo-1.3-order plots for $Co_2(CO)_8$ reaction with $P(i\text{-}Pr)_3$ in CH_2Cl_2 at 25 °C. The concentrations of base are 3.0×10^{-2} M (▲) ($k_{obsd} = (4.38 \pm 0.43) \times 10^{-2}$ $M^{-0.3}$ s^{-1}), 7.00×10^{-2} M (●) ($k_{obsd} = (7.61 \pm 0.26) \times 10^{-2}$ $M^{-0.3}$ s^{-1}), and 9.00×10^{-2} M (■) ($k_{obsd} = (8.55 \pm 0.49) \times 10^{-2}$ $M^{-0.3}$ s^{-1}).

pressure of purified nitrogen over the solutions during kinetic runs.

Results

Reaction with $P(t\text{-}Bu)_3$. Reaction of $Co_2(CO)_8$ with $P(t\text{-}Bu)_3$ at 25 °C in CH_2Cl_2 follows a first-order rate law. No dependence on concentration of base is observed. The first-order rate constant was determined to be 1.7×10^{-2} s^{-1}. Table I gives calculated rate constants for various base concentrations. Addition of air to the base solution before reaction has no effect on the observed rate of reaction. Saturation of both carbonyl and base solutions with CO prior to reaction results in a decrease in reaction rate (Figure 1).

Reaction with $P(CH_2CH_2CN)_3$. Reaction of $Co_2(CO)_8$ with $P(CH_2CH_2CN)_3$ in CH_2Cl_2 at 25 °C also follows a first-order rate law, with no dependence on concentration of base. Table II gives calculated rate constants for various base concentration. The first-order rate constant was determined to be 1.3 $\times 10^{-2}$ s^{-1}. Addition of air to the base solution before reaction does not have any effect on observed kinetics, but saturation of both solutions before reaction with CO decreases rate of reaction slightly.

Reaction with $P(i\text{-}Pr)_3$. Reaction of $Co_2(CO)_8$ with $P(i\text{-}Pr)_3$ in CH_2Cl_2 was studied at both 25 and 0 °C. The observed order in $Co_2(CO)_8$ appeared to change with temperature. At 25 °C, the observed order in carbonyl was approximately 1.3 while at 0 °C an order in $Co_2(CO)_8$ of about 1.5 was observed. At 0 °C, the reaction order in base appears to be 1.0, while at 25 °C an order of approximately 0.6 is observed. Pseudo-1.3-order plots for data at 25 °C and pseudo-1.5-order plots for data at 0 °C are shown in Figures 2 and 3, respectively. Addition of air to the base solution before reaction did not affect the observed rate.

Discussion

Both the basicity and steric requirement of a phosphine may affect the character of its substitution reaction with $Co_2(CO)_8$. The bases employed in this study were chosen so that the two effects could be separated as much as possible. It is then possible to assign any differences in reactivity to either a steric or nucleophilic origin.

The kinetics of reaction of $Co_2(CO)_8$ with $P(n\text{-}Bu)_3$ at 25 °C in CH_2Cl_2 have previously been reported.[23] So that the effect of steric requirement could be determined, reactions of $Co_2(CO)_8$ with $P(i\text{-}Pr)_3$ and $P(t\text{-}Bu)_3$ were examined and compared with the results for reaction with $P(n\text{-}Bu)_3$. These trialkylphosphines all possess very similar basicities, whereas the steric requirements vary widely. To determine the effect of the basicity of the phosphine on the course of substitution reactions, we studied the reaction of $P(CH_2CH_2CN)_3$ with $Co_2(CO)_8$ at 25 °C and compared these with results from reaction of $P(n\text{-}Bu)_3$. These two bases have very similar steric properties, but the basicity of $P(CH_2CH_2CN)_3$ is much lower than that of $P(n\text{-}Bu)_3$. The cone angle was used as the measure of relative steric requirement,[24] and the A_1 carbonyl stretching frequency of $Ni(CO)_3L$ was taken as indicative of relative basicity.[24] A lower value of the stretching frequency corresponds to a more basic phosphine. Values for these parameters are given in Table III.

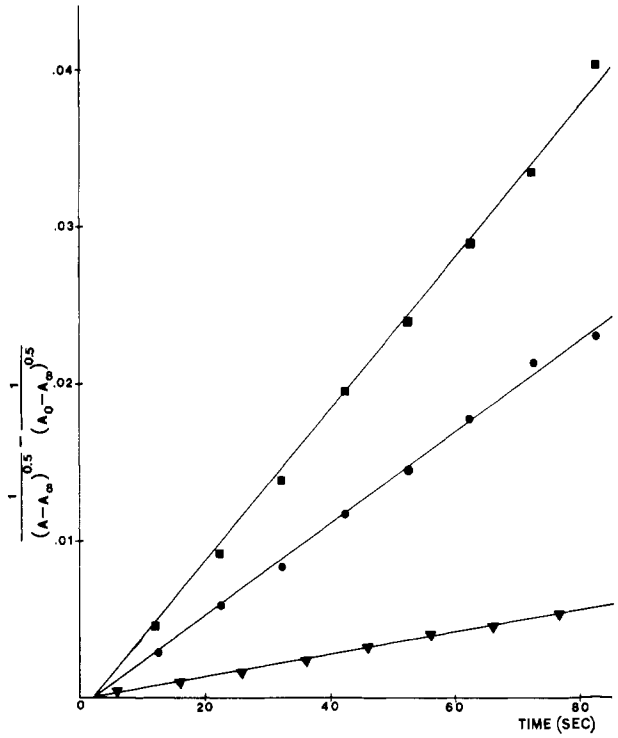

Figure 3. Pseudo-1.5-order plots for $Co_2(CO)_8$ reaction with $P(i\text{-}Pr)_3$ in CH_2Cl_2 at 0 °C. The base concentrations are 10^{-2} M (▲) ($k_{obsd} = (0.28 \pm 0.03) \times 10^{-2}$ $M^{-0.5}$ s^{-1}), 3.2×10^{-2} M (●) ($k_{obsd} = (1.10 \pm 0.08) \times 10^{-2}$ $M^{-0.5}$ s^{-1}), and 5.3×10^{-2} M (■) ($k_{obsd} = (1.58 \pm 0.13) \times 10^{-2}$ $M^{-0.5}$ s^{-1}).

Table III. Cone Angle and Electronic Parameters for Phosphines[24]

PR_3	θ, deg	ν_{A_1}, cm^{-1}
$P(t\text{-}Bu)_3$	182	2056.1
$P(i\text{-}Pr)_3$	160	2056.2
$P(n\text{-}Bu)_3$	132	2060.3
$P(CH_2CH_2CN)_3$	132	2077.9

Dissociative Loss of CO. The reaction of $Co_2(CO)_8$ with $P(t\text{-}Bu)_3$ is an example of a reaction proceeding by a rate-determining CO dissociation from $Co_2(CO)_8$. The first-order rate law, containing no term in entering ligand, is consistent with a rate-determining loss of CO, followed by rapid reaction to form $Co_2(CO)_7P(t\text{-}Bu)_3$. It is consistent also with the observed inhibition of reaction rate upon addition of CO. Since $Co_2(CO)_6[P(t\text{-}Bu)_3]_2$ is formed as final product, a second CO dissociation from $Co_2(CO)_7P(t\text{-}Bu)_3$ must occur. This coor-

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dinatively unsaturated species then reacts with excess $P(t\text{-}Bu)_3$ in solution to give the final product. The proposed reaction mechanism is given in eq 1–4. The kinetic behavior for

$$Co_2(CO)_8 \rightarrow Co_2(CO)_7 + CO \quad (1)$$

$$Co_2(CO)_7 + L \rightarrow Co_2(CO)_7L \quad (2)$$

$$Co_2(CO)_7L \rightarrow Co_2(CO)_6L + CO \quad (3)$$

$$Co_2(CO)_6L + L \rightarrow Co_2(CO)_6L_2 \quad (4)$$

reaction of $Co_2(CO)_8$ with $AsPh_3$,[17] i.e., first-order dependence on $Co_2(CO)_8$ concentration, no dependence on base concentration, and inhibition of rate by addition of CO, is identical with that reported here for the reaction of $Co_2(CO)_8$ with $P(t\text{-}Bu)_3$. The observed first-order rate constant of 1.7×10^{-2} s^{-1} compares favorably with that of 2.0×10^{-2} s^{-1} reported for reaction with $AsPh_3$.

The reaction of $Co_2(CO)_8$ with $P(CH_2CH_2CN)_3$ also appears to be occurring via rate-determining CO dissociation form $Co_2(CO)_8$. First-order dependence on $Co_2(CO)_8$ with no dependence on concentration of entering base is observed. Inhibition of the reaction in the presence of added CO is not as great as in the $P(t\text{-}Bu)_3$ reaction. The reason for this decreased effect in reaction of $P(CH_2CH_2CN)_3$ is not known. However, it may lie in the relative rates of reaction of the phosphine and CO with the $Co_2(CO)_7$ intermediate.

Radical Pathway. We have previously proposed[17,23] that reaction of $Co_2(CO)_8$ with $P(n\text{-}Bu)_3$ occurs by a radical chain mechanism which is shown in eq 5–14. Reaction of $Co_2(CO)_8$

$$Co_2(CO)_8 + L \rightleftharpoons Co_2(CO)_8L \quad (5)$$

$$Co_2(CO)_8L \rightarrow Co(CO)_3L\cdot + Co(CO)_4\cdot + CO \quad (6)$$

$$Co(CO)_3L\cdot + Co_2(CO)_8 \rightarrow Co(CO)_3L^+ + Co_2(CO)_8^-\cdot \quad (7)$$

$$Co_2(CO)_8^-\cdot \rightarrow Co(CO)_4^- + Co(CO)_4\cdot \quad (8)$$

$$Co(CO)_3L^+ + L \rightarrow Co(CO)_3L_2^+ \quad (9)$$

$$Co(CO)_4\cdot \rightarrow Co(CO)_3\cdot + CO \quad (10)$$

$$Co(CO)_3\cdot + L \rightarrow Co(CO)_3L\cdot \quad (11)$$

$$Co(CO)_3L\cdot + Co(CO)_4\cdot \rightarrow Co_2(CO)_7L \quad (12)$$

$$Co(CO)_3L\cdot + Co(CO)_3L\cdot \rightarrow Co_2(CO)_6L_2 \quad (13)$$

$$Co(CO)_4\cdot + Co(CO)_4\cdot \rightarrow Co_2(CO)_8 \quad (14)$$

with $P(i\text{-}Pr)_3$ appears to provide another example of a reaction occurring by this mechanism. Formation of ionic products and nonintegral order in both $Co_2(CO)_8$ and $P(i\text{-}Pr)_3$ are suggestive of this type of process. Consistent with observations made for $P(n\text{-}Bu)_3$, the observed order in $Co_2(CO)_8$ varies with temperature. However, in contrast to the reaction with $P(n\text{-}Bu)_3$ which has a half-life of approximately 70 ms at 25 °C, reaction with $P(i\text{-}Pr)_3$ is relatively slow. A slower rate of reaction may be accounted for at two points in the mechanism. The preequilibrium equation (5) would be expected to be shifted to the left due to the greater steric bulk of $P(i\text{-}Pr)_3$ relative to $P(n\text{-}Bu)_3$. There would result a smaller steady-state concentration of the associated species $Co_2(CO)_8L$. However, while this could account for the initial slowness of the rate, it does not completely account for the slower overall rate. If the preequilibrium were the only step affected by steric factors, once a few of the radicals are formed and the electron transfer in eq 7 occurs, radicals would also be formed as a result of reactions 8, 10, and 11. Since $P(i\text{-}Pr)_3$ is slightly more basic than $P(n\text{-}Bu)_3$, the electron transfer from $Co(CO)_3P(i\text{-}Pr)_3\cdot$ should be slightly more favorable than electron transfer from $Co(CO)_3P(n\text{-}Bu)_3\cdot$. Once radicals were being formed by the electron transfer, the reaction should proceed at the same rate or slightly faster than observed for $P(n\text{-}Bu)_3$ reactions. Since this is not observed, it is necessary to postulate a steric hindrance to the electron transfer. For an outer-sphere electron transfer to occur, the two species must have an appropriate orientation relative to each other. With the bulkier $P(i\text{-}Pr)_3$ ligand on the radical, there could be a steric hindrance to approach of the radical to $Co_2(CO)_8$ so that the electron transfer rate would also be slower.

Formation of the disubstituted dinuclear species as a minor product of the reaction must also be accounted for. One possibility is that CO dissociation from $Co_2(CO)_8$, as proposed for reaction with $P(t\text{-}Bu)_3$, occurs at a rate competitive with the radical process. However, experimental observations suggest this is not the case. There is none of the monosubstituted dinuclear compound formed, only the disubstituted. In a separate experiment, it was found $Co_2(CO)_7P(i\text{-}Pr)_3$ reacts with $P(i\text{-}Pr)_3$ to yield $CO_2(CO)_6[P(i\text{-}Pr)_3]_2$ with a first-order rate constant of about 1.2×10^{-3} s^{-1} at 25 °C. Since the rate constant for CO dissociation from $Co_2(CO)_8$ is about 1.5×10^{-2} s^{-1} at 25 °C, any $Co_2(CO)_7P(i\text{-}Pr)_3$ formed as a result of the CO dissociation from $Co_2(CO)_8$ should be seen as a product of the reaction.

The second possible source of disubstituted dinuclear compound is from recombination of the radicals $Co(CO)_3P(i\text{-}Pr)_3\cdot$ (eq 13). Results from a computer-modeling study[17] of this radical chain mechanism have shown that if the rate of electron transfer (eq 7) is not at least as rapid as the recombination in eq 13, the dinuclear disubstituted compound accumulates to an observable concentration. It would be expected that the rate of this recombination would also be slowed due to steric interaction between the substituted radicals. Flash photolysis studies[25] of $Co_2(CO)_8$ and $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ have shown that recombination of two $Co(CO)_3P(n\text{-}Bu)_3\cdot$ radicals is about 5 times slower than recombination of two $Co(CO)_4\cdot$ radicals. That the disubstituted dinuclear compound is formed in observable concentration suggests that the rate of electron transfer is more affected by steric hindrance than is the rate of radical recombination.

The lack of any effect of oxygen on the rate of reaction is puzzling. In contrast, the presence of oxygen causes a definite slowing of the rate of reaction of $Co_2(CO)_8$ with $P(n\text{-}Bu)_3$. The absence of any effect of oxygen may be due to the slowness of the chain process in the $P(i\text{-}Pr)_3$ case. The effect of oxygen presumably arises from interaction of the radical with oxygen as in eq 15.

$$Co(CO)_3L\cdot + O_2 \rightleftharpoons Co(CO)_3LO_2\cdot \quad (15)$$

Effect of Base on Reaction Pathway. As has been shown in reaction of $Co_2(CO)_8$ with $P(n\text{-}Bu)_3$, a radical chain mechanism giving rise to a very fast rate of reaction is possible in reaction of $Co_2(CO)_8$ with phosphines. However, these results have also shown that this mechanism may operate at a slower rate as in the reaction with $P(i\text{-}Pr)_3$. Alternatively a different reaction pathway may be followed as in reaction with $P(t\text{-}Bu)_3$ or $P(CH_2CH_2CN)_3$. In all of these cases, the only factor varied is the nature of the base.

It can reasonably be assumed that, due to the rapid nature of the chain process, the radical chain mechanism will dominate if it can occur. However, if the radical chain process is for some reason inhibited at any point, the CO dissociative mechanism will be operative. There are two points in the chain mechanism where the nature of the base can be a critical factor. The first of these is the preequilibrium and chain initiation steps, 5 and 6, respectively. For the preequilibrium to lead successfully to chain initiation, i.e., formation of radical

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species, the interaction between the attacking base and $Co_2(CO)_8$ must be sufficiently strong to cause metal–metal bond rupture. Both the nucleophilicity and steric requirement of the base are important in determining how successful the preequilibrium will be in initiating the chain process. If the base is so bulky that a close approach to the metal center is prevented, the interaction will be too weak to cause metal–metal bond homolysis. In addition, even with the assumption that the base can successfully approach the metal, the nucleophilicity of the base must be sufficiently high to induce breaking of the metal–metal bond.

Reaction of $Co_2(CO)_8$ with $P(i\text{-}Pr)_3$ has been discussed as an example of a reaction in which a steric hindrance to the preequilibrium appears to be operating. Reaction of $Co_2(CO)_8$ with $P(t\text{-}Bu)_3$ is most likely prevented from occurring by a radical chain pathway because the approach of $P(t\text{-}Bu)_3$ to the metal center is blocked by the bulkiness of the ligand. The low nucleophilicity of $P(CH_2CH_2CN)_3$ can account for the lack of any radical chain mechanism in its reactions with $Co_2(CO)_8$. This base can attack the metal center but is not a sufficiently strong base to initiate the chain process by causing rupture of the Co–Co bond.

A second place in the radical chain mechanism where the nature of the base can be an important consideration is the electron-transfer step (eq 7). The rate of electron transfer should be sensitive to the energy requirement for oxidation of the radical species $Co(CO)_3L\cdot$. The potentials for reversible oxidation of neither $Co_2(CO)_8$ nor the radicals $Co(CO)_3L\cdot$ are known. However, it may be reasonably argued that radicals substituted with strongly electron-donating ligands should undergo oxidation reactions more readily than radicals substituted with less electron-donating ligands. This is observed in the reaction of $Co_2(CO)_8$ with $P(CH_2CH_2CN)_3$. When solutions of $Co_2(CO)_8$ and $P(CH_2CH_2CN)_3$ are flash photolyzed immediately after mixing, there is no evidence for formation of ionic products, as would be expected from an electron transfer. Radicals are formed in the flash, yet no electron-transfer process appears to occur. We suggest that the electron-transfer process is energetically unfavorable due to the low basicity of $P(CH_2CH_2CN)_3$.

Several experimental observations suggest that steric hindrance to electron transfer can be important. As previously discussed, the results of the reaction of $Co_2(CO)_8$ with $P(i\text{-}Pr)_3$ can be accounted for in terms of a reduced electron-transfer rate. Further evidence for a steric effect comes from the results of the reaction of $Co_2(CO)_8$ with $P(t\text{-}Bu)_3$. When solutions of $Co_2(CO)_8$ and $P(t\text{-}Bu)_3$ are flashed immediately after mixing, there is no evidence for formation of ionic products, which would be expected from an electron-transfer process. The argument that the cation, $Co(CO)_3[P(t\text{-}Bu)_3]_2^+$, might be unstable due to the bulkiness of the $P(t\text{-}Bu)_3$ groups may be valid. However, the anion $Co(CO)_4^-$ should be stable under these conditions, and no evidence for the presence of $Co(CO)_4^-$ is seen. Flashing the solution must certainly produce $Co(CO)_4\cdot$ radicals. In view of the known lability of $Co(CO)_4\cdot$ with respect to substitution by phosphines, $Co(CO)_3P(t\text{-}Bu)_3\cdot$ must also be formed. Due to the high basicity of $P(t\text{-}Bu)_3$, electron transfer from $Co(CO)_3P(t\text{-}Bu)_3\cdot$ to $Co_2(CO)_8$ should be energetically favorable. That such a process does not appear to be occurring suggests that some other barrier to electron transfer is present. The most probable explanation is a steric effect.

Mattson and Bailey[27] have measured the self-exchange electron-transfer rate constant for the couple $(RNC)_6Mn^+/(RNC)_6Mn^{2+}$. Rate constants are reported to be 6.4×10^5 $M^{-1}\ s^{-1}$ when R is ethyl and 4×10^4 $M^{-1}\ s^{-1}$ when R is *tert*-butyl. Chan[28] reports the self-exchange rate between $Fe(phen)_3^{3+}/Fe(phen)_3^{2+}$ and $Fe(4,7\text{-cyclohexylphen})_3^{3+}/Fe(4,7\text{-cyclohexylphen})_3^{2+}$ to be 6×10^6 and 4×10^5 $M^{-1}\ s^{-1}$, respectively. The decreased rates for the complexes of bulkier ligands are proposed to be the result of a steric inhibition to electron transfer. Kochi and co-workers[29,30] have proposed a steric effect on electron transfer in two systems. Steric effects on the rate of formation of the charge-transfer complex $[R_4Sn^+\cdot TCNE^-]$ are seen. As the bulkiness of the R groups on Sn increases, the rate of formation of the charge-transfer complex decreases. In addition, the rate of electron transfer from R_4Sn compounds to $IrCl_6^{2-}$ is dependent upon the steric requirement of R groups which are attached to the tin center.

In summary, the present work has shown that two mechanisms are possible for the substitution reactions of $Co_2(CO)_8$. One of these involves a rate-determining CO dissociation. The coordinatively unsaturated intermediate rapidly adds nucleophile to give substituted dinuclear products. A second pathway for substitution involves an associative attack at $Co_2(CO)_8$, forming an intermediate $Co_2(CO)_8L$. This intermediate undergoes relatively rapid metal–metal bond homolysis. Through an outer-sphere electron-transfer reaction, the $Co(CO)_3L\cdot$ species thus formed initiates a radical chain process leading to formation of the ionic products.

The nucleophilicity and steric requirement of the base determine which of the two possible pathways will be followed and the rate of the reaction. Results of this work have shown that in order for a rapid radical chain reaction to be observed, the base must have a high nucleophilicity and small steric requirement. If one of these criteria is not met, the alternative CO dissociative pathway will be followed. $P(t\text{-}Bu)_3$ with a large steric requirement and $P(CH_2CH_2CN)_3$ with a low nucleophilicity each react with $Co_2(CO)_8$ via the CO dissociative pathway. For bases of intermediate steric requirement, e.g., $P(i\text{-}Pr)_3$, reaction may occur by the radical chain mechanism but at a rate much slower than observed with the smaller base $P(n\text{-}Bu)_3$.

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