Table II. Comparison of Rate Constants (25 °C) for Reductions by $Fe(CN)_6^{4-}$ and $Ru(NH_3)_6^{2+}$

			k_{Ru}/k_{Fe}	
oxidant	k_{Fe}, s^{-1}	k_{Ru},[a] s^{-1}	obsd[b]	calcd[c]
$Co(NH_3)_5O_2CCH_3^{2+}$	3.7×10^{-4}	0.10	2.8×10^2	2.2×10^2
$Co(NH_3)_5py^{3+}$	1.5×10^{-2} [d]	6.56[e]	4.4×10^2	1.7×10^2
$Ru(NH_3)_5py^{3+}$	9.7×10^3 [d]	4.5×10^6 [d]	4.6×10^2	1.7×10^2

[a] Calculated from k_{obsd}/Q_{IP}, where k_{obsd} is the measured second-order rate constant and Q_{IP} is the association constant between ruthenium and cobalt complexes calculated from eq 4 and 5. [b] Ratio of first-order rate constants given in columns 2 and 3. [c] Calculated from the Marcus relationship; see text. [d] Reference 4. [e] Reference 12.

ligand. Therefore, the observed increase in k_{et} with decreasing pK_a can be ascribed, at least in part, to the increased reduction potential of the cobalt(III) center.[14] Turning to a consideration of the intrinsic barrier, it must be recognized that, in the inner-sphere reduction of cobalt(III)[15] and chromium(III)[16] complexes, outward motion of the ligands along the z axis obtains in order to bring down the energy of the d_{z^2} orbital that accepts the electron. Such motion, part of the inner-shell reorganization energy, depends on the σ-donor ability of the ligands.[11] As the σ-donor strength increases, more energy is necessary for outward motion and the rate constant decreases. It was noted[11] that the above treatment does not depend on whether the reaction is inner sphere or outer sphere and that the σ-bonding theory of nonbridging ligand effects[17] is also applicable to outer-sphere reactions. Therefore, the observed increase in k_{et} with decreasing pK_a of the carboxylate ligand (which measures the σ-bonding strength of the ligand) can be ascribed, at least in part, to the intrinsic barrier. Whether the thermodynamic or the intrinsic barrier is more important in governing the observed trends cannot be ascertained because the reduction of the cobalt(III) complexes is irreversible and thus their reduction potentials are not known.

It is instructive to compare the rate constant for the reduction of $Co(NH_3)_5O_2CCH_3^{2+}$ by $Fe(CN)_6^{4-}$ with the corresponding value for the reduction by $Ru(NH_3)_6^{2+}$. The pertinent data are listed in Table II together with the values for the reductions of $Co(NH_3)_5py^{3+}$ and $Ru(NH_3)_5py^{3+}$ by $Fe(CN)_6^{4-}$[4] and $Ru(NH_3)_6^{2+}$.[12] The measured rate constants for reductions by $Fe(CN)_6^{4-}$ correspond to the elementary first-order processes for internal electron transfer within the ion pairs. In contrast, the measured rate constants for reductions by $Ru(NH_3)_6^{2+}$ are composite constants ($k_{et}Q_{IP}$) that include the desired rate constants for internal electron transfer and the ion-pair formation constant. Therefore, values of k_{et} for the reductions by $Ru(NH_3)_6^{2+}$ were calculated from the measured[4,12] second-order rate constants and the values of Q_{IP} (0.21, 0.10, 0.16 M^{-1}) estimated by utilization of eq 4 and 5. It will be seen (column 4 of Table II) that the ratio of the rate constants for internal electron transfer in $Ru(NH_3)_6^{2+}$ and in $Fe(CN)_6^{4-}$ reactions are independent of the nature of the oxidant. This is the expected result if the three reactions under consideration obey the Marcus relationship since the properties that depend upon the identity of the oxidant cancel out when ratios are taken. In fact, the ratio can be calculated from the known reduction potentials[18,19] and rate constants for self-exchange[18,20,21] of the $Fe(CN)_6^{3-/4-}$ and $Ru(NH_3)_6^{3+/2+}$ couples. The results of the calculations are listed in column 5 of Table II, and it will be seen that they are in excellent agreement with observed values (column 4). It is noteworthy that the calculation is equally successful for oxidants that are σ-electron acceptors ($Co(NH_3)_5O_2CCH_3^{2+}$ and $Co(NH_3)_5py^{3+}$) and for $Ru(NH_3)_5py^{3+}$, a π-electron acceptor (in all cases the reductants are π-electron donors). The agreement between observed and calculated ratios indicates that the electronic factors[22] in the exchange and cross-reactions are similar and, banning some fortuitous cancellation, that all of these electron-transfer reactions proceed at or near the adiabatic regime.

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Registry No. $Fe(CN)_6^{4-}$, 13408-63-4; $Co(NH_3)_5O_2CCH_3^{2+}$, 16632-78-3; $Co(NH_3)_5O_2CC_6H_5^{2+}$, 30931-77-2; $Co(NH_3)_5O_2C$-*o*-$C_6H_4NO_2^{2+}$, 62714-55-0; $Co(NH_3)_5O_2C$-*m*-$C_6H_4NO_2^{2+}$, 62714-56-1; $Co(NH_3)_5O_2C$-*p*-$C_6H_4NO_2^{2+}$, 36445-08-6; $Co(NH_3)_5O_2CCH_3^{2+}|Fe(CN)_6^{4-}$, 91443-82-2; $Co(NH_3)_5O_2CC_6H_5^{2+}|Fe(CN)_6^{4-}$, 91443-83-3; $Co(NH_3)_5O_2C$-*o*-$C_6H_4NO_2^{2+}|Fe(CN)_6^{4-}$, 91443-84-4; $Co(NH_3)_5O_2C$-*m*-$C_6H_4NO_2^{2+}|Fe(CN)_6^{4-}$, 91443-85-5; $Co(NH_3)_5O_2C$-*p*-$C_6H_4NO_2^{2+}|Fe(CN)_6^{4-}$, 91443-86-6.

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(21) The measured second-order rate constants divided by the ion-pair formation constants calculated from eq 6 and 7 yield first-order rate constants for internal electron transfer in $Ru(NH_3)_6^{3+}/Ru(NH_3)_6^{2+}$ and in $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ of 4.4×10^5 s^{-1} and 1.4×10^6 s^{-1}, respectively.

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Comparison between Carbonyl Derivatives of Palladium and Those of Nickel and Platinum

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Palladium is an important element in several catalytic carbonylations.[1] Some features of the chemistry of palladium carbonyl complexes appear to be unusual with respect both to its congener elements in the nickel subgroup and to other transition elements. In particular, some structural, spectroscopic, and chemical properties of palladium carbonyl complexes cannot easily be explained by the usual mechanism of synergic σ–π contributions to the Pd–CO bond.

Recent work in these laboratories led to the convenient preparations of palladium and platinum carbonyl complexes[2] with the same valence electron count and presumably the same molecular structure, thus allowing a comparison of properties to be made within elements belonging to the same vertical sequence (a group trend).

Experimental Section

All of the reactions reported in this paper were carried out under an atmosphere of prepurified carbon monoxide or dinitrogen, as specified. Solvents were dried prior to use by the conventional pro-

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Table I. ^{195}Pt NMR Spectra and Carbonyl Stretching Vibrations of Platinum(II) Derivatives in Thionyl Chloride

compd	δ[a]	ν_{CO}, cm^{-1}
cis-$Pt(CO)_2Cl_2$	614	2179, 2136
trans-$Pt(CO)_2Cl_2$	729	2150
$Pt_2(CO)_2(\mu\text{-}Cl)_2Cl_2$	1507, 1511	2139

[a] At high frequency of ^{195}Pt = 21.4 MHz.

cedures. The platinum dimer was prepared as previously described.[2c] The IR spectra were measured with a Perkin-Elmer Model 283 instrument equipped with a grating. ^{195}Pt NMR spectra were measured at 21.4 MHz with a XL 100 spectrometer using the ^{19}F external lock. About 20000 transients were accumulated for each spectrum by using a pulse width of 30 μs. A spectrum of the platinum dimer $Pt_2(CO)_2Cl_4$ was also measured at 53.6 MHz with a Bruker WH 250 spectrometer. In the latter case, a mixture of $SOCl_2$ and $CDCl_3$ was used as solvent and the spectra were recorded with the deuterium lock with CD_2Cl_2 as internal reference.

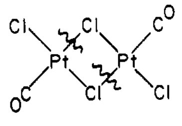
Reaction of $Pt_2(CO)_2(\mu\text{-}Cl)_2Cl_2$ with CO. The platinum(II) dimer (0.50 g, 0.85 mmol) in thionyl chloride (ν_{CO}, 2139 cm^{-1}) was treated with carbon monoxide at atmospheric pressure at about 22 °C in a flask protected from light. After a few minutes of stirring, the IR spectrum showed the band at 2150 cm^{-1} due to *trans*-$Pt(CO)_2Cl_2$. The reaction conditions were maintained for about 24 h (until the IR spectrum showed the bands of *cis*-$Pt(CO)_2Cl_2$ at 2179 and 2136 cm^{-1}, exclusively). If carbon monoxide was evacuated from the reaction flask at the initial stages of the reaction, when the cis isomer was not yet present, and substituted with dinitrogen, the system reverted to the original dimer. In a control gas-volumetric experiment carried out at 20.5 °C, 82% of the expected amount of CO for the stoichiometry of eq 2 was found to be absorbed.

Preparation of *trans*-$Pt(CO)_2Cl_2$. The platinum(II) dimer $Pt_2(CO)_2Cl_4$ (0.330 g, 0.56 mmol) was suspended in thionyl chloride (15 cm^3) and reacted with CO at atmospheric pressure at about −80 °C. The reaction was monitored by IR spectroscopy and was found to proceed gradually to the formation of the trans isomer. After about 2 h, the mixture consisted approximately of equal amounts of the starting material and the trans isomer. The reaction was found to be complete after about 10 h. Heptane, which had been pretreated with a few drops of $SOCl_2$ and cooled at ca. −80 °C, was added to favor the precipitation of the trans isomer. The latter was isolated by filtration at dry ice temperature, dried briefly in vacuo (0.225 g, 62% yield), and kept under nitrogen at dry ice temperature. Anal. Calcd for $C_2Cl_2O_2Pt$: CO, 17.4. Found (by gas-volumetric determination of the CO displaced by PPh_3): CO, 16.6. The solid appears to be stable for several days at dry ice temperature; on the other hand, the compound was unstable at room temperature, especially under exposure to normal daylight and was converted to a mixture of dimer and cis isomer. A freshly prepared solution of the trans isomer under dinitrogen showed the ^{195}Pt NMR signal indicated in Table I. The carbonylation of the platinum dimer was also monitored by ^{195}Pt NMR spectrometry. The application of the three independent techniques (IR, analyses, and ^{195}Pt NMR) led to the unequivocal identification of the species present in solution.

Carbonylation of $PtCl_4^{2-}$. A 0.122 M solution of $(NBu_4)_2PtCl_4$ in thionyl chloride was stirred under carbon monoxide at atmospheric pressure at 22.5 °C. After 24 h, the IR spectrum showed bands at 2098 ($Pt(CO)Cl_3^-$) and at 2136 and 2179 ($Pt(CO)_2Cl_2$) cm^{-1}.

Results and Discussion

The more recently acquired information[2] on palladium(II) and platinum(II) carbonyl derivatives and the data available in the literature can be used to compare the three elements in the nickel subgroup, according to their oxidation states.



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Oxidation State II. The behavior of the dimers $M_2(CO)_2(\mu\text{-}Cl)_2Cl_2$ (M = Pd, Pt) toward CO differs considerably on going from palladium to platinum.

$$Pd_2(CO)_2(\mu\text{-}Cl)_2Cl_2 + 2CO \nrightarrow 2Pd(CO)_2Cl_2 \tag{1}$$

$$Pt_2(CO)_2(\mu\text{-}Cl)_2Cl_2 + 2CO \rightleftharpoons 2\textit{trans}\text{-}Pt(CO)_2Cl_2 \tag{2}$$

$$\textit{trans}\text{-}Pt(CO)_2Cl_2 \rightarrow \textit{cis}\text{-}Pt(CO)_2Cl_2 \tag{3}$$

No conditions were found to carry out reaction 1. Since d^8 palladium(II) is usually faster than platinum(II) in substitution reactions,[3] the failure to observe reaction 1 is not due to a kinetic barrier. Taking into account the accepted values[4] of Pd–Cl$_{br}$ (br = bridging) and Pd–Cl$_t$ (t = terminal) bond energies as 48 and 62 kcal, respectively, a simple calculation shows that the Pd(II)–CO$_t$ bond energy would have to be at least 34 kcal for the enthalpy change of reaction 1 to become approximately zero. The value of about 24 kcal for the Pd(II)–CO$_t$ bond energy calculated[2e] from the thermodynamic parameters of the formation of $Pd_2(CO)_2Cl_4$ from $PdCl_2$ and CO suggests that reaction 1 should not proceed to any appreciable extent, in agreement with experiment. On the contrary, the platinum dimer reacts at room temperature with CO at atmospheric pressure to *cis*-$Pt(CO)_2Cl_2$. The trans isomer was identified as the kinetically controlled product of the carbonylation, and at about −80 °C, it was isolated and characterized by analysis and IR and ^{195}Pt NMR techniques; see Table I.

It is interesting to note that the platinum dimer shows two ^{195}Pt resonances, separated by about 4 ppm. The nonequivalence of the two resonances suggests that we are dealing with two compounds whose chemical environment must be very slightly different. The ^{195}Pt NMR spectra are very sensitive indeed, as shown by the fact that the resonances of the $[Pt(CO)X_3]^-$ anions span a range of about 2200 ppm on going from Cl to I.[5a-c] The suggestion can therefore be made that two $SOCl_2$-solvated dimers exist in solution. Another possibility is the stacking of dimer molecules, as suggested for the $Pd_2(PBu_3)_2Cl_4/Pt_2(PBu_3)_2Cl_4$ exchange reaction.[5d] The existence in solution of cis and trans isomers of the dimer is excluded by the high stereospecificity of the reaction leading to the initial formation of trans isomer exclusively and on the basis of the unique carbonyl stretching vibration observed in the IR spectrum of the dimer.

In reactions 2 and 3 we see formation of a new Pt(II)–CO$_t$ bond replacing one Pt–Cl$_{br}$ bond per platinum. The overall enthalpy change of the reaction will also reflect a change from Pt–Cl$_{br}$ to Pt–Cl$_t$, but the reaction proceeds in spite of unfavorable entropic contribution (assuming solvation energies are about the same for reagents and products). The uncertainties existing[6] about Pt–Cl bond energies and the numerous assumptions that have to be made render the assessment of a

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lower limit of the $Pt(II)–CO_t$ bond energy a rather difficult task.

Complementary to these results is the fact that the anionic species of palladium(II) and platinum(II), $[M(CO)Cl_3]^-$, behave differently with respect to CO substitution by Cl^-. While the palladium species reacts promptly[2c] with the stoichiometric amount of NH_2R_2Cl in dichloromethane to give $PdCl_4^{2-}$, stable solutions of $[Pt(CO)Cl_3]^-$ in thionyl chloride can be obtained from $Pt(CO)_2Cl_2$ even with an excess of Cl^- under carbon monoxide, and solutions of $[Pt(CO)Cl_3]^-$ in *concentrated* hydrochloric acid can be handled (ν_{CO} 2113 cm^{-1}, CaF_2 cell).

$$[M(CO)Cl_3]^- + Cl^- \rightarrow CO + MCl_4^{2-} \qquad M = Pd \qquad (4)$$

That kinetic barriers are not involved in these observations is shown by the fact that $PtCl_4^{2-}$ as its tetrabutylammonium derivative was found to react with CO to give an equilibrium mixture of $[Pt(CO)Cl_3]^-$ and $Pt(CO)_2Cl_2$, by operating in $SOCl_2$ as solvent:

$$PtCl_4^{2-} + CO \rightarrow [Pt(CO)Cl_3]^- + Cl^- \qquad (5)$$

$$[Pt(CO)Cl_3]^- + CO \rightleftharpoons Pt(CO)_2Cl_2 + Cl^- \qquad (6)$$

These results suggest that there is a rather drastic increase of the $M(II)–CO_t$ bond energy on going from palladium to platinum.

Cleavage of the chloride bridge of the platinum(II) dimer to give *trans*-$Pt(CO)_2Cl_2$ initially is in line with the known strong trans effect of carbon monoxide as a ligand,[7] as shown in **1**. The isomerization to the cis isomer is presumably due to a negative enthalpy change arising from better solvation of the more polar isomer and probably also to a more stable arrangement of the σ-bonded carbonyl groups being trans to two electronegative ligands such as Cl. Earlier data[2] suggest that π-back-donation makes a negligible contribution to the ground-state stabilization of the Pt–CO bond. A similar suggestion was offered[8] for tertiary phosphines bonded to platinum(II). We believe that the unusually high ν_{CO} values observed for platinum(II) complexes (and even more so for palladium(II)) are related to the σ-electron flowing from CO to the metal. It is well recognized now that both π-[9] and σ-effects[10] can play a role in the control of the activation parameters of the five-coordinate intermediate in substitutions of square-planar platinum(II) complexes. Our data are of only qualitative value to be used for any further comment on the trans effect. We are, however, planning to elucidate this problem further.

Oxidation State I. Some carbonyl derivatives of d^9 palladium(I) are known, namely the $[Pd_2(\mu\text{-}CO)_2Cl_4]^{2-}$ anion[11] (ν_{CO} 1980 w, 1916 s cm^{-1} in *sym*-$C_2H_2Cl_4$,[2e] Pd–C–Pd(av) = 85.2 (3)°[11b]), the presumably polymeric[2e,11a,12] $[Pd(CO)Cl]_n$, $Pd_4(CO)_4(OAc)_4$,[13] and $Pd_2(CO)Cl_2(Ph_2AsCH_2AsPh_2)_2$.[14] All of these compounds have *carbonyl bridges* exclusively. This is particularly relevant for the chloride anionic complex, this being the first halo–carbonyl derivative with bridging CO's rather than bridging Cl's.[15] Although the Pd–Pd contact in $[Pd_2(\mu\text{-}CO)_2Cl_4]^{2-}$ is 2.697 (5) Å only, a recent theoretical treatment[11c] has indicated that no metal–metal bond is present in the anion. This result is even more striking considering that the corresponding platinum derivative $Pt_2(CO)_2Cl_4^{2-}$ has terminal CO and Cl groups in a Pt–Pt-bonded dimeric structure.[16] The polymeric $[Pd(CO)Cl]_n$, which is obtained by reduction of $PdCl_2$ or $Pd_2(CO)_2Cl_4$ with CO in acetic anhydride,[2e] is characterized by a carbonyl stretching vibration at 1975 cm^{-1} attributed to the bridging carbonyl groups. Alternating chloride and carbonyl bridges are the most reasonable structural assumption for this compound.[2e,11a] It thus appears that the wavenumber values of bridging carbonyl groups in palladium complexes are out of the range typical of most transition-metal carbonyl complexes. Intriguing is the fact that a second category of carbonyl-bridged dimers of palladium exists, exemplified by the so-called A-frame,[17a] $Pd_2(CO)Cl_2(Ph_2AsCH_2AsPh_2)_2$ (ν_{CO} 1720 cm^{-1}, Pd–C–Pd = 119°) for which a dimetalated formaldehyde bonding arrangement of d^8 palladium(II) has been proposed.[17b,c]

Oxidation State 0. No binary carbonyl derivatives of palladium(0) are known, and only a limited number of tertiary-phosphine-substituted carbonyl complexes have been reported, namely $Pd(CO)(PPh_3)_3$,[18] $Pd_4(\mu\text{-}CO)_6(PBu_3)_4$,[19] $Pd_7(\mu\text{-}CO)_3(\mu_3\text{-}CO)_4(PMe_3)_7$,[20] and $Pd_{10}(\mu\text{-}CO)_8(\mu_3\text{-}CO)_4(PBu_3)_6$.[19] The doubly and triply bridging carbonyl groups in the polynuclear species are characterized by carbonyl absorptions[18] at about 1960 cm^{-1} in benzene solution. Two different solid modifications of $Pt(CO)(PPh_3)_3$ have been reported, both of slightly distorted tetrahedral geometry, one belonging to space group $P3$[21] and the other to space group $P2_1/n$.[22] A few neutral tertiary-phosphine-substituted carbonyl derivatives of platinum(0) have been reported,[23a,b] and some anionic binary cluster species of platinum generally having both terminal and bridging carbonyl groups are also known.[23c,f]

Considerations on Pd–CO Bonds. On going from platinum to palladium, ν_{CO} is observed to increase, and with the exception of $Pd(CO)(PPh_3)_3$, terminal CO groups disappear as the oxidation state of the metal decreases. This suggests that π-back-donation is unessential for the stabilization of $Pd–CO_t$ bonds. For elements such as palladium and possibly silver, $M–CO_t$ bonds may be expected to vary their stability as a function of the oxidation state, reaching a maximum at some intermediate relatively *high* oxidation state, possibly II for both palladium and platinum. In polynuclear complexes of Pd(I) and Pd(0), there is a mechanism other than π-back-donation

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to relieve electronic charge, namely the μ-CO arrangement. This permits charge delocalization by a σ-type of bonding. Thus, the 16-electron compound $[Pd_2(\mu\text{-}CO)_2Cl_4]^{2-}$ is more stable with respect to the other two possibilities: the 16-electron species $[Pd_2(CO)_2Cl_4]^{2-}$ (all groups terminal with a metal–metal bond, as experimentally found[16] in the case of platinum) and the 18-electron complex $[Pd_2(CO)_2(\mu\text{-}Cl)_2Cl_2]^{2-}$. The latter is clearly unfavorable for electron-rich metals lacking an efficient mechanism of π-back-donation.

If a σ-type of bonding is essentially operative for palladium in its binding to CO, decreasing the oxidation state does not necessarily correspond to the stabilization of Pd–CO_t bonds. Further support to this assumption can be obtained from the experimentally observed low stability[24] of $Pd(CO)_4$ as compared to that of $Ni(CO)_4$ in spite of the lower enthalpy of sublimation of palladium (91 kcal/mol) with respect to that of nickel (103 kcal/mol).[25]

Note should also be taken of the apparently peculiar nature of chemisorbed CO on palladium. On this metal, bridging carbonyl groups have been detected spectroscopically[26] and suggested to contribute considerably to the coverage of the surface. This sets an example of how the information from molecular homogeneous systems can sometimes be transferred with some confidence to heterogeneous systems.

These considerations, together with our earlier findings on gold(I) carbonyl complexes,[27] suggest that for late and heavy transition elements, especially those of d^{10} configuration, the mechanism of stabilization of the M–CO_t bond is substantially one of σ-donation to the metal. This makes the carbonyl carbon especially prone to nucleophilic attack, as evidenced by the high reactivity of these carbonyl complexes toward water and amines.[28]

Once certain requirements are met (availability of empty valence orbitals with subsequent sufficient Lewis acidity of the metal center), σ-bonding of CO should not be too surprising, though still uncommon. A few examples of compounds of this type, for which a simple description in terms of σ-bonding appears to be in order, are the d^0 $ZrCp_2(CO)H_2$ and $HfCp_2(CO)H_2$[29] (ν_{CO} 2044 and 2036 cm^{-1}, respectively) and $BH_3(CO)$[30] (ν_{CO} 2165 cm^{-1}).

Summary

Contrary to $Pd_2(CO)_2(\mu\text{-}Cl)_2Cl_2$, which is unreactive toward CO, the corresponding platinum(II) dimer reacts promptly with CO at atmospheric pressure and room temperature to give *cis*-$Pt(CO)_2Cl_2$. It has been shown that the reaction proceeds via the intermediate formation of the kinetically controlled trans isomer, which has been isolated and characterized by analysis, IR spectroscopy, and ^{195}Pt NMR spectroscopy. These results are discussed within the framework of the general problem of metal–terminal CO bonds for elements of the nickel triad. Other things being equal, the Pd–CO_t bond appears to be inherently weaker than the corresponding bonds for nickel and platinum, due to lack of an efficient π-back-bonding mechanism. Thus, palladium shows little transitional behavior in its combination with CO. This result is expected in view of the position of the metal in the periodic table but has been frequently neglected.

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Note Added in Proof. The compound $Pd_{10}(CO)_{14}(PBu_3)_4$ was recently shown[31] to have two terminal carbonyl groups. In our hands, *trans*-$Pt(CO)_2Cl_2$ gave a mixture of *cis*-$Pt(CO)_2Cl_2$ and $Pt_2(CO)_2Cl_4$ by sublimation under reduced pressure (ca. 5 × 10^{-2} mmHg); cf. ref 32.

Registry No. $Pt(CO)_2(\mu\text{-}Cl)_2Cl_2$, 17522-99-5; *trans*-$Pt(CO)_2Cl_2$, 62841-60-5; *cis*-$Pt(CO)_2Cl_2$, 15020-32-3; $(NBu_4)_2PtCl_4$, 21790-80-7; $(Pt(CO)Cl_3^-)$, 21710-57-6; Pt, 7440-06-4; Ni, 7440-02-0; Pd, 7440-05-3.

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Kinetics of the Acid Dissociation of the Copper(II) and Nickel(II) Complexes of 5,7-Dioxo-1,4,8,11-tetraazacyclotetradecane

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The acid dissociation kinetics of open-chain polyamine complexes have been extensively studied,[1-9] and the topic has been reviewed.[10] Currently there is considerable interest in the kinetics and mechanism of the acid dissociation of macrocyclic polyamine complexes.[11-20] For 14-membered tetraaza

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