Communication

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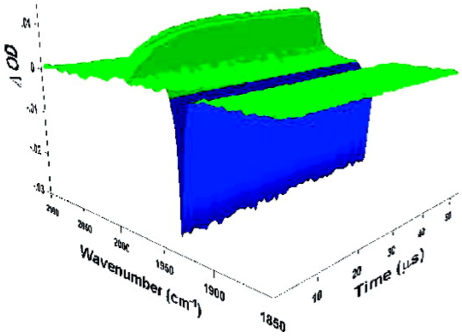

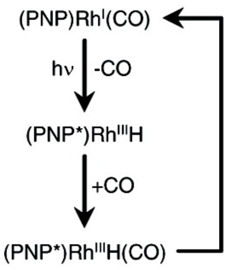

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Metal-Dependent Reactivity Differences for Transients Formed By Flash Photolysis of (PNP)M(CO), M = Co and Rh

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The recent synthesis[1] of the low-coordinate Co(I) pincer ligand complex (PNP)Co, where PNP = $[(^{t}Bu_2PCH_2SiMe_2)_2N]^{-1}$, invites comparison with its rhodium homologue. Several features come to mind; for example, agostic interactions are generally much more common for the 4d and 5d analogues of these later transition metals. Furthermore, rhodium normally is the much more reducing species and shows a more frequent occurrence of two-electron redox change, given that Co(II) is a commonly found oxidation state. These differences may in part be attributed to the smaller d orbital splittings of 3d metals that leads to more frequent occurrence of unpaired electrons when coordination number is low; for example, (PNP)Co has a triplet ground state.[1] The potential impact of an "open shell" (incomplete spin pairing) on reactivity thus adds an additional dimension of interest.[2−4] We report here the reaction dynamics of CO addition to (PNP)Co, as well as to the transient produced by flash photolysis of (PNP)Rh(CO), an excitation which would ordinarily be expected to produce the transient (PNP)Rh. The results reveal the considerably greater complexity of the Rh system, which originates from the general periodic features described above, and serve to test for any rate retardation owing to spin differences between these 3d and 4d homologues.

(PNP)Co(CO) is formed in time of mixing by adding CO (1 atm) to isolable, three-coordinate (PNP)Co in benzene or cyclohexane solvent. The adduct does not detectably dissociate when the CO is removed by evacuation, so it has a high formation constant. (PNP)-Co shows no agostic interaction with PNP substituents[1] and shows no evidence (X-ray structure or changed ^{1}H NMR or visible/UV spectrum) of bonding interactions with benzene or cyclohexane solvents. This is due to the triplet nature of (PNP)Co and is reminiscent of an earlier observation on a transient Co complex.[5]

Flash photolysis (355 nm) of (PNP)Co(CO) (1.8×10^{-4} M) in cyclohexane solution under 1 atm CO using time-resolved optical (TRO) detection generates transient spectral changes with increased absorbance at 420 nm and bleaching at 460 and 547 nm. Transient decay at all three wavelengths followed single-exponential kinetics over ~5 half-lives. The resulting k_{obs} values were statistically equivalent at $7.3(\pm1.5) \times 10^{3}$ s^{-1}. A plot of k_{obs} values determined at varying CO pressure[6] and monitored at 420 nm shows a first-order dependence on [CO], establishing (eq 1) an overall rate law k^{Co}[Co][CO] with $k^{Co} = 9.3(\pm0.2) \times 10^{5}$ M^{-1} s^{-1}. Point-by-point determination of the electronic spectrum of the transient shows a band in satisfactory agreement with the 415 nm band recorded for authentic three-coordinate (PNP)Co in cyclohexane. Thus, the transient being trapped by CO is assigned as the electronic ground state of (PNP)Co.

$$\text{(PNP)Co(CO)} \underset{k^{Co}}{\overset{h\nu}{\rightleftarrows}} \text{(PNP)Co} + \text{CO} \qquad (1)$$

In a separate experiment under analogous conditions, flash photolysis (355 nm) of (PNP)Co(CO) using time-resolved infrared (TRIR) detection establishes that the ν_{CO} at 1885 cm^{-1} is bleached and then undergoes exponential recovery. A plot of k_{obs} versus [CO] is linear with a second-order rate constant of $8.0(\pm1.5) \times 10^{5}$ M^{-1} s^{-1} in cyclohexane solution, in satisfactory agreement with the value from the TRO experiment. No other transient ν_{CO} band was seen, consistent (eq 1) with photoexcitation labilizing the CO ligand under these conditions.

The corresponding TRO study of (PNP)Rh(CO) (2.4×10^{-4} M) under 1 atm of CO in cyclohexane shows an initial bleach at 360 nm and a transient absorbance at 470 nm. The latter shows (Scheme 1) single-exponential decay over ~5 half-lives with a rate constant of $5.7(\pm0.2) \times 10^{4}$ s^{-1}. A plot of k_{obs} values determined at varying [CO] is linear with a second-order rate constant of $6.3(\pm1.0) \times 10^{6}$ M^{-1} s^{-1}.

However, the temporal behavior for re-formation of the (PNP)-Rh(CO) band at 360 nm is quite different. Variable CO pressure studies of its growth establish zero-order dependence of k_{obs} on [CO], with a first-order rate constant $k^{Rh} = 3.3(\pm0.3) \times 10^{1}$ s^{-1}. The capture of the first transient by CO thus does not re-form (PNP)Rh(CO), but rather some new intermediate, **B**, which then only slowly transforms into (PNP)Rh(CO).

Single frequency TRIR studies establish the decline of intensity of the (PNP)Rh(CO) ν_{CO} band at 1931 cm^{-1} (confirmed independently by decay of this band when (PNP)Rh(CO) is irradiated at 77 K in a methylcyclohexane matrix) and that its recovery is complete, with a rate constant of $3.9(\pm0.2) \times 10^{1}$ s^{-1}. This rate constant was independent of [CO], fully consistent with the TRO observations. Continuous photolysis of (PNP)Rh(CO) under 1 atm N_2 in cyclohexane generates (PNP)Rh(N_2), ν_{NN} at 2090 cm^{-1}, characterized by spectroscopy and a crystal structure determination.[7]

Time-resolved step-scan FTIR monitoring (Figure 1) of a solution of (PNP)Rh(CO) (1.5×10^{-3} M) in *n*-heptane under 1.9 atm of CO, flashed at 355 nm, shows an instantaneous bleach of the 1931 cm^{-1} CO stretch of the carbonyl, with no new ν_{CO} bands being observed immediately after the laser flash in the region probed (1820−2250 cm^{-1}). This rules out that the transient produced, **A** (Figure 1), is an excited state of (PNP)Rh(CO). DFT calculations predict that the IR frequency of O-bound (PNP)Rh(OC) would be 1920 cm^{-1}, so **A** is unlikely to be this linkage isomer. The subsequent exponential growth of two new, comparably strong bands at 1991 and 2001 cm^{-1} (Figure 1) was monitored at varying concentrations of added CO, and the resulting k_{obs} values showed first-order dependence on [CO] over the concentration range of 4.1 to 22.6 mM. The resulting second-order rate constants ($k_{1991cm^{-1}} = 6.3(\pm0.6) \times 10^{6}$ M^{-1} s^{-1} and $k_{2001cm^{-1}} = 6.5(\pm0.7) \times 10^{6}$ M^{-1}

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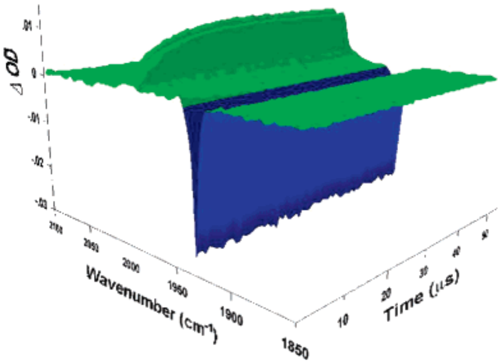
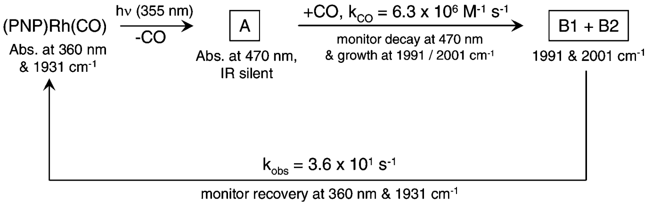
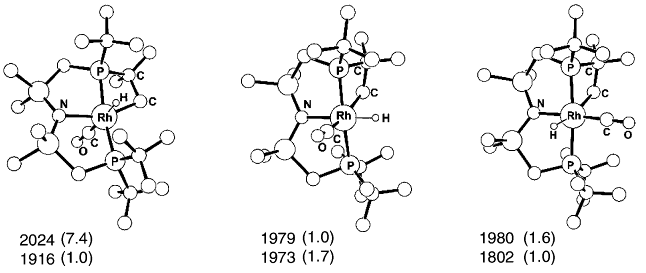


Figure 1. Transient FTIR spectra recorded after 355 nm excitation of (PNP)Rh(CO) in *n*-heptane, showing the growth (green) of absorptions **B1** and **B2** of (PNP*)RhH(CO), without significant regeneration of (PNP)Rh(CO) (blue) on the microsecond time scale.

Scheme 1



Scheme 2. Relative Isomer Energies (*E*) and Unscaled HRhCO Vibrational Frequencies (Intensities)



2024 (7.4)
1916 (1.0)

1979 (1.0)
1973 (1.7)

1980 (1.6)
1802 (1.0)

1 (+12.6 kcal/mol) **2** (0.0 kcal/mol) **3** (+4.4 kcal/mol)

s^{-1}) are, within experimental error, indistinguishable and identical to that determined by the TRO study for the decay of the 470 nm transient band. Moreover, the fact that the slower return process to re-form (PNP)Rh(CO) is CO-independent means that the transient already contains the components of the final product. The two observed frequencies, **B1** and **B2**, are too similar to indicate a dicarbonyl composition. The 60−70 cm^{-1} increase in frequency for **B1** and **B2** versus (PNP)Rh(CO) is consistent with a carbonyl complex of Rh(III) and hence indicates some oxidative addition event has occurred prior to CO addition; the IR-silent transient **A** is not simply $(PNP)Rh^{I}$. We have evaluated the hypothesis that IR bands **B1** and **B2** are due to isomeric monocarbonyl adduct(s) of what has been established independently[7] as the structure of the ground state of "(PNP)Rh", which has one ^{t}Bu methyl C−H oxidatively added to the metal, giving $[\eta^4\text{-}{}^{t}Bu_2PCH_2SiMe_2NSiMe_2CH_2P^{t}Bu(CMe_2CH_2)]RhH$, $(PNP^*)Rh^{III}H$. This has been done by DFT calculations of structures, energies and IR frequencies, and intensities of all three possible isomers (Scheme 2).

The vibrations shown for **2** and **3** are essentially pure CO (higher frequency) and pure Rh−H motions, while those for **1** are strongly mixed. Because both observed frequencies (**B1** and **B2**) have the same decay rate, while reductive elimination of H and CH_2 in **3** (in which they are mutually trans) should be slower than from **2**, we believe that only **2** is formed, and that this accounts for the transient IR spectra. The observed 10 cm^{-1} IR frequency difference agrees satisfactorily with the calculated frequency difference (6 cm^{-1}) in **2**. IR intensities for the two bands assigned to isomer **2** are calculated to be 1:1.7, in satisfactory agreement with experiment. (PNP*)RhH has a Y-shaped geometry with ∠C−Rh/H 74.1°, and the observed isomer involves addition of CO in the large ∠N−Rh−H 142.9°.

These results show that the transient produced by photodissociation of CO from (PNP)Rh(CO) promptly oxidatively adds an internal ^{t}Bu C−H bond to give the ground state structure observed elsewhere[7] for "(PNP)Rh" (i.e., (PNP*)RhH).[8] It does not oxidatively add *n*-heptane solvent and has a <10 ns lifetime as a three-coordinate species, in contrast to (PNP)Co. No ν_{Rh-H} transient IR band was observed for (PNP*)RhH by TRIR spectroscopy, as expected due to its extremely weak oscillator strength, which was confirmed by DFT calculations. Carbon monoxide adds selectively to (PNP*)RhH to give one stereoisomer, which more slowly reductively eliminates H and C(sp^3) to form $(PNP)Rh^{I}(CO)$. The rate of addition of CO to triplet (PNP)Co to give singlet (PNP)Co(CO) is ∼3−4 orders of magnitude slower than diffusion limits[9] and is even slower than that for addition of CO to the five-coordinate Rh^{III} intermediate (PNP*)RhH. These observations suggest that the triplet spin state of (PNP)Co strongly inhibits the rate of CO addition.

The results reported here affirm that the tendency to undergo H−C(sp^3) oxidative addition is much less for an electron-rich cobalt than for its rhodium analogue, making authentic, three-coordinate (PNP)Rh undetectable on our time scale. The half-life for reductive elimination of H and C(sp^3) from these carbonyl adducts is nevertheless short on the laboratory synthetic time scale, and the strong π-acid CO ligand alters the thermodynamics for Rh oxidation state change to favor Rh^{I} in the CO adduct versus Rh^{III} in the CO-free species (PNP*)RhH.

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Supporting Information Available: Full computational and experimental details and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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