

stereoelectronic effects may be particularly important.²³

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Addition of Methylene Chloride and Methyl Iodide to the Phenyl Ring of Aryl Imido/Amido Complexes of Rhodium¹

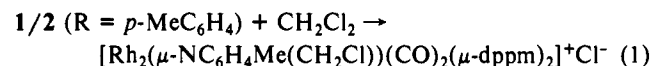
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Growing interest in late-transition-metal oxo, imido, amido, alkoxo, and aryloxo complexes has resulted in the preparation of a number of complexes in which these ligands are highly basic.²⁻⁴ The resulting reaction chemistry is dominated by the nucleophilic or basic properties of the heteroatom center. In this communication we report a novel and unusual reaction of a late-transition-metal aryl imido/amido complex which indicates that the high electron density at the nitrogen center has been distributed out into the aryl ring, inducing high nucleophilic reactivity at the para ring position.

Standing tautomeric mixtures of Rh₂(μ-NR)(CO)₂(μ-dppm)₂ and Rh₂(μ-NHR)(CO)₂(μ-dppm-H)(μ-dppm) (**1/2**) [R = *p*-MeC₆H₄, dppm = bis(diphenylphosphino)methane, dppm-H = bis(diphenylphosphino)methanide]^{1,2b} in CH₂Cl₂ leads to a slow reaction yielding a new product formulated as [Rh₂(μ-NC₆H₄Me(CH₂Cl))(CO)₂(μ-dppm)₂]⁺Cl⁻ (**3**) (eq 1).⁵ The re-



action takes several days to reach ca. 90% completion and involves an unusual formal addition of CH₂Cl⁺ to the para position of the imido/amido ring of **1/2** (R = *p*-MeC₆H₄).

The ¹H NMR spectrum of **3** is quite distinctive with a clear A₂B₂ pattern for the former aryl ring upfield of the aromatic region. An upfield shift is also observed for the ring methyl group, indicating a loss of aromaticity in the ring. The ³¹P NMR spectra of **3** are symmetric and suggest dynamic exchange⁶ or undetectable

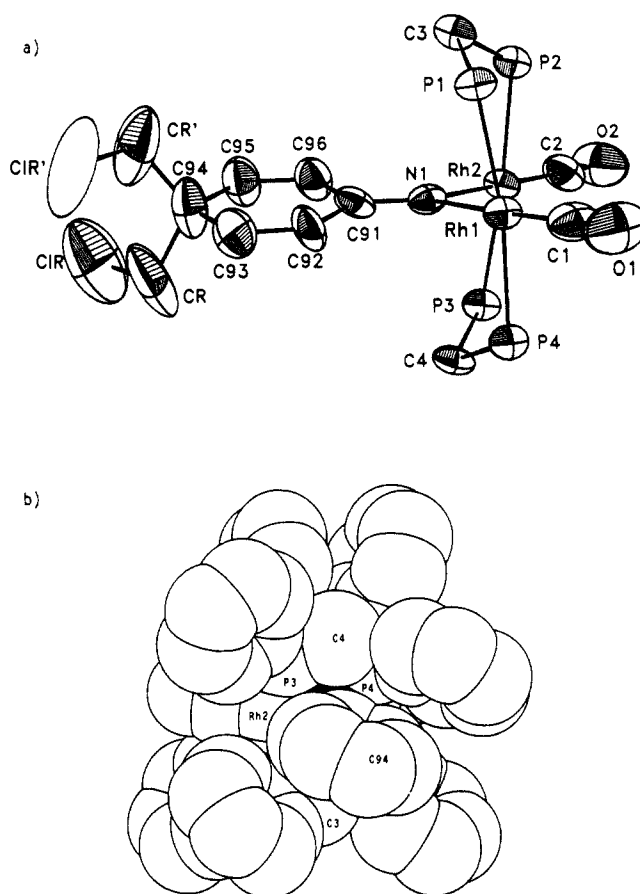


Figure 1. Drawings of the cationic portion of **3**, [Rh₂(μ-NC₆H₄Me-(CH₂Cl))(CO)₂(μ-dppm)₂]⁺Cl⁻. (a) ORTEP, 50% probability ellipsoids. Phenyl rings omitted. The open ellipsoid of ClR' represents the minor position for the CH₂Cl group (see text). Selected bond distances (Å): Rh1-N, 2.05 (1); Rh2-N, 2.04 (1); N1-C91, 1.29 (2); C91-C92, 1.46 (2); C91-C96, 1.48 (2); C92-C93, 1.31 (2); C96-C95, 1.32 (2); C93-C94, 1.48 (2); C95-C94, 1.52 (3); C94-CR, 1.58 (3); C94-CR', 1.50 (3); CR-CIR, 1.67 (2); CR'-CIR', 1.48 (4). Selected bond angles (deg): Rh1-N-Rh2, 97.3 (4); Rh1-N-C91, 129.1 (9); Rh2-N-C91, 133.5 (9); N1-C91-C92, 123 (1); N1-C91-C96, 122 (1); C92-C91-C96, 115 (1); C91-C92-C93, 121 (1); C91-C96-C95, 122 (1); C92-C93-C94, 127 (2); C96-C95-C94, 125 (1); C93-C94-C95, 109 (1); C93-C94-CR, 105 (2); C93-C94-CR', 109 (2); C95-C94-CR, 105 (2); C95-C94-CR', 111 (2); CR-C94-CR', 117 (2); C94-CR-CIR, 112 (2); C94-CR'-CIR', 116 (2). (b) PLUTO, van der Waals radii. Substituents CR, CR', Cl, and Cl' omitted from C94. Darkened area is N1.

differences in the phosphorus atom environments.

An ORTEP diagram of the cationic portion of **3** is shown in Figure 1a.⁷ The ring methyl group and the CH₂Cl group are disordered. This results in full occupancy of both carbon atom positions CR and CR' but only partial occupancy of the chlorine atom positions. Occupancy refinement of ClR and ClR' suggests a 35% and 65% distribution with ClR being the major position. An inspection of the N-C and C-C distances and angles (figure caption) clearly shows the quinoid-like structure represented in I.

As expected from the above results, methyl iodide also adds to the aryl ring of **1/2** (R = *p*-MeC₆H₄). The reaction is complete within minutes, and the only detectable product is [Rh₂(μ-

(6) The NMR spectra (¹H and ³¹P) do show some broadening at -80 °C.

(7) Crystal data for **3**, C₄₀H₄₃Cl₂NO₂P₄Rh₂·CH₂Cl₂ (fw = 1306.64): monoclinic (C2/c), a = 37.20 (1) Å, b = 12.827 (3) Å, c = 26.497 (6) Å, β = 97.35 (2)°, V = 12538 Å³, d_{calcd} = 1.38, Z = 8. Data (Mo Kα) were collected on a CAD4 diffractometer. The structure was solved by Patterson methods (SHELXS-86; Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Godard R., Eds.; Oxford University Press: London, 1985; pp 175-189) and refined by full matrix least squares refinement (SDP) to R = 0.065 and R_w = 0.087 for 3858 absorption-corrected observations with F_o² > 2σ(F_o²) and 673 variables. Details will be provided in a forthcoming full paper.

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(5) Data for [Rh₂(μ-NC₆H₄Me(CH₂Cl))(CO)₂(μ-dppm)₂]⁺Cl⁻ (**3**): IR (CH₂Cl₂) 1990 (m), 1975 cm⁻¹ (s); ¹H NMR (300 MHz, CD₂Cl₂) δ 7.1-7.7 (m, 40 H, Ph), 5.73 and 5.53 (2 d, J_{HH} = 10 Hz, 2 × 2 H, C₆H₄), 3.41 (s, 2 H, CH₂Cl), 3.22 and 3.06 (2 m, 2 × 2 H, PCH₂P), 1.09 (s, 3 H, CH₃); ³¹P NMR (121 MHz, CD₂Cl₂) δ 22.8 (dm, J_{RHP} = 136.6 Hz); ¹³C{¹H} NMR (75 MHz, CD₂Cl₂) δ 52.0 (s, CH₂Cl), 25.0 (s, CH₃), 21.3 (m, PCH₂P).



$\text{NC}_6\text{H}_4\text{Me}_2(\text{CO})_2(\mu\text{-dppm})_2]^+\text{I}^-$ (4) (eq 2). The spectral data⁸ $1/2$ ($\text{R} = p\text{-MeC}_6\text{H}_4$) + $\text{MeI} \rightarrow$
 $[\text{Rh}_2(\mu\text{-NC}_6\text{H}_4\text{Me}_2)(\text{CO})_2(\mu\text{-dppm})_2]^+\text{I}^-$ (2)

for 4 are similar to those for 3. Treating $1/2$ ($\text{R} = \text{Ph}$) with MeI gives a product analogous to 4,⁹ but at least one other, as yet unidentified, product is also formed.

These results suggest a high degree of charge density in the imido and/or amido aryl ring. The formal positive charge on the nitrogen of the amido tautomer would not be expected to lead to such high charge density. On the other hand, the availability of the nitrogen lone pair in the imido tautomer makes possible the contribution of resonance form II (see above), which could lead to the observed reactivity.¹⁰ However, the major resonance form should have most of the charge density on the nitrogen. This is consistent with the observed nitrogen protonation of $1/2$ by acidic species.^{1,2b,11} Why do we observe here CH_2Cl^+ and Me^+ addition to the ring and not to the nitrogen? The answer may be, at least partly, steric inaccessibility. A "space-filling" PLUTO diagram of 3 (Figure 1b) shows the derivatized imido ligand in a "pocket" formed by the dppm ligands. The structure of 3 is common to dppm A-frame complexes, and the parent imido complex is expected to have a similar structure with restricted access to the nitrogen. Consistent with steric control, we find no evidence of ring addition in the reaction of the analogous dmpm complex [dmpm = bis(dimethylphosphino)methane] with CH_2Cl_2 .¹² The lower steric demand of the dmpm ligand may allow reaction to occur at the nitrogen.

Another consideration for these electron-rich species is electron transfer.¹³ A single-electron-transfer (SET) mechanism¹⁴ for the ring addition is a definite possibility. We have treated $1/2$ with various oxidizing agents (I_2 , Br_2 , O_2) in an attempt to test for this. NMR evidence does suggest the formation of a ring addition product in the O_2 reaction. In addition, we have found that $1/2$ ($\text{R} = p\text{-MeC}_6\text{H}_4$) undergoes a chemically reversible (cyclic voltammetric time scale) oxidation in THF at very low potentials (-0.6 V vs SCE). These and further results will be presented fully in a forthcoming full paper.

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Supplementary Material Available: Table of fractional coordinates and thermal parameters (non-hydrogen) for 3 (2 pages). Ordering information is given on any current masthead page.

(8) Data for $[\text{Rh}_2(\mu\text{-NC}_6\text{H}_4\text{Me}_2)(\text{CO})_2(\mu\text{-dppm})_2]^+\text{I}^-$ (4): IR (CH_2Cl_2) 1988 (m), 1973 cm^{-1} (s); ^1H NMR (300 MHz, CD_2Cl_2) δ 7.2-7.5 (m, 40 H, Ph), 5.47 and 5.40 (2 d, J_{HH} = 10.4 Hz, 2 \times 2 H, C_6H_4), 3.01 (m, 4 H, PCH_2P), 0.92 (s, 6 H, CH_3); ^{31}P NMR (36 MHz, CD_2Cl_2) δ 22.1 (dm, J_{RhP} = 137.9 Hz).

(9) On the basis of the observation of an A_2B_2 pattern and a high-field methyl group similar to that of 3 and 4.

(10) An equivalent but opposite resonance form has been proposed for the addition of H^- to the para position of the tolylcarbyne ring of $[\text{Os}(\text{CR})(\text{CO})_2(\text{PPh}_3)_2]^+$ ($\text{R} = p\text{-MeC}_6\text{H}_4$). The resulting vinylidene complex is closely related to our product 3: Roper, W. R.; Waters, J. M.; Wright, L. J.; Van Meurs, F. J. *Organomet. Chem.* **1980**, *201*, C27-C30.

(11) Proton attack on the dppm-H ligand of the amido tautomer is also possible.

(12) Work in progress.

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The Role of Vibrational Energy in the Ultrafast Photodissociation of $\text{Cr}(\text{CO})_6$

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In this paper, an investigation is presented of the photodissociation of $\text{Cr}(\text{CO})_6$ and the subsequent reaction dynamics of the photoproducts using picosecond transient Raman spectroscopy. Contrary to the common perception that nonequilibrium vibrational energy does not contribute to condensed-phase reactions, it is found instead that the appearance time of the thermally equilibrated $\text{Cr}(\text{CO})_5$ photoproduct is rate limited by vibrational energy decay. This result has important implications to recent ultrafast studies of the photochemistry of $\text{Cr}(\text{CO})_6$. Transient absorption experiments have discovered¹⁻³ that photoexcitation of $\text{Cr}(\text{CO})_6$ results in the formation of solvated $\text{Cr}(\text{CO})_5$ which appears in a time of ≤ 0.8 ps in hydrocarbon solvents. However, in contrast to these results, a controversy now exists due to the experiments of Spears et al.^{4,5} where transient picosecond infrared data has been interpreted to show that solvated $\text{Cr}(\text{CO})_5$ appears to be produced by several different mechanisms on a much slower time scale. In contrast to this interpretation, time-dependent shifts in the absorption maximum of solvated $\text{Cr}(\text{CO})_5$ have been attributed^{2,6} to vibrational energy relaxation which occurs⁶ in 17 ps.

The results reported in this paper remove the present controversy by directly probing the vibrational coordinates of the photoproducts using transient Raman spectroscopy. The experimental apparatus has been previously described in detail.⁷⁻¹⁰ Figure 1 shows the picosecond transient Raman spectra obtained at various optical delays for 266-nm excitation of $\text{Cr}(\text{CO})_6$ in cyclohexane. Two 5-ps pulses at 266 nm are used in this experiment. The first pulse photodissociates $\text{Cr}(\text{CO})_6$, and the second probes the resonance Raman spectrum of $\text{Cr}(\text{CO})_5$. The advantage of detecting resonance Raman scattering at this wavelength is that the ultraviolet absorption band of $\text{Cr}(\text{CO})_5$ is very strong¹⁴ ($\epsilon = 3 \times 10^4$ $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ at 240 nm) and relatively insensitive to solvent interactions. The spectra contain only pure transient Raman bands after removal of solvent and ground-state $\text{Cr}(\text{CO})_6$ bands using a spectrum differencing technique. This was achieved by alternately exciting the sample with a single interrogation laser pulse or a double pump-probe laser pulse sequence. The pure transient spectrum shown in Figure 1 is obtained by subtracting the one-pulse background spectrum from that obtained in the double-pulse sequence.

Comparing frames A-D in Figure 1, it is readily apparent that a single transient appears with a time scale of roughly 100 ps. The metal-CO stretch at 381 cm^{-1} and the CO vibration at 1935

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