Homogeneous Catalytic Carbonylation of Nitroaromatics. 9. Kinetics and Mechanism of the First N—O Bond Cleavage and Structure of the η^2-ArNO Intermediate

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*Summary: The reaction between Ru(dppe)(CO)₃ and ArNO₂ produced CO₂ and the new complex Ru(dppe)-(CO)₂(η²-ONAr), which was shown by X-ray crystallography to contain a π-bound nitrosoarene ligand. Kinetic studies using a variety of substituents on the nitroarene established that the reaction was first order in each reagent and were consistent with an electron-transfer process during the rate-determining step.*

One of the promising alternatives to the use of phosgene for the production of isocyanates and carbamates is the metal-catalyzed carbonylation shown in eq 1.[1] Ruthenium,[2-15] rhodium,[8,16,17] and palladium[18-22] com-

$$ArNO_2 + 3CO + MeOH \rightarrow$$
$$ArNHC(O)OMe + 2CO_2 \quad (1)$$
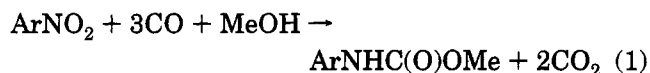
plexes exhibit the highest catalytic activity among the transition metals for this reaction. Despite an expanding knowledge[11-14] of the mechanism of this reaction

using Ru(dppe)(CO)₃ (**1**), where dppe = 1,2-bis(diphenylphosphino)ethane, as the catalyst, there existed no direct experimental evidence of the mechanism of the initial reaction between the nitroaromatic and the zerovalent metal complex to produce the unusual metallacyclic complex **2**, shown in eq 2. In this communica-

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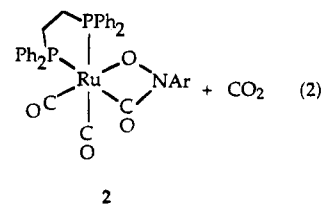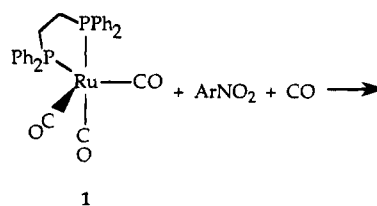
tion we describe the isolation of the intermediate nitrosoarene complex, and we provide kinetic evidence that its formation occurs via a rate-determining electron-transfer mechanism.

The kinetics of the reaction between **1** and ArNO₂ under N₂ at 25.0 °C in THF were monitored using infrared spectroscopy and established that an intermediate, identified as Ru(dppe)(CO)₂(η²-ONAr), was formed. The stability of this species was greatly enhanced by the presence of electron-withdrawing substituents on

® Abstract published in *Advance ACS Abstracts,* October 1, 1994.
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(23) Synthesis and spectroscopic data for Ru(dppe)(CO)₂(η²-ONC₆H₃-ClCF₃): Ru(dppe)(CO)₃ (0.28 g, 0.48 mmol) was loaded into the reaction flask in a glovebox, and the vessel was removed from the box. A THF solution (10 mL) of 5-chloro-2-nitrobenzotrifluoride (0.328 g, 1.45 mmol) was deoxygenated with a stream of N₂ and added to the reaction flask via cannula. The reaction mixture was kept at 0 °C, and N₂ was constantly bubbled through the solution, which turned from canary yellow to dark red. Upon completion of the reaction (as determined by IR spectroscopy) the volume was reduced to ca. 3 mL, and dry hexane (15 mL) was added to the reaction mixture at −78 °C. The orange-red precipitate was collected on a glass frit at −78 °C, washed several times with hexanes, and dried in vacuo to yield 250 mg of product. IR (cm⁻¹, KBr): ν_{CO} 2028 (s), 1960 (s). ¹H NMR (ppm, CD₂Cl₂): 2.43 (m, 4H, CH₂), 7.33 (m, 10H, Ar H), 7.60 (m, 5H, Ar H), 8.01 (m, 3H, Ar H). ³¹P{¹H} NMR (ppm relative to 85% H₃PO₄, CD₂Cl₂): 67.7 (d, J_{PP} = 18.2 Hz), 49.1 (d, J_{PP} = 18.1 Hz). ¹³C{¹H} NMR (excluding most aromatic carbons, ppm, CD₂Cl₂): 24.97 (dd, J_{CP1} = 16 Hz, J_{CP2} = 31.7 Hz, CH₂), 28.17 (dd, J_{CP1} = 11.1 Hz, J_{CP2} = 28.0, CH₂), 116.6 (q, J_{CF} = 30.55 Hz), 124 (q, J_{CF} = 273.4 Hz, CF₃), 165.57 (d, J_{CF} = 36.96 Hz, ipso C), 191.23 (dd, J_{CP1} = 75.57 Hz, J_{PC2} = 112.3 Hz, CO), 198.3 (d, J_{PC1} = 13.42 Hz). ¹⁹F NMR (ppm relative to CFCl₃, CD₂Cl₂): −59.89 (s, CF₃). Mass spectrum (¹⁰²Ru, *m/e*): 766 (parent ion). Anal. Calcd for C₃₆H₂₉Cl₃F₃NO₃P₂Ru: C, 50.89; H, 3.44; N, 1.65. Found: C, 50.68; H, 3.56; N, 1.69.
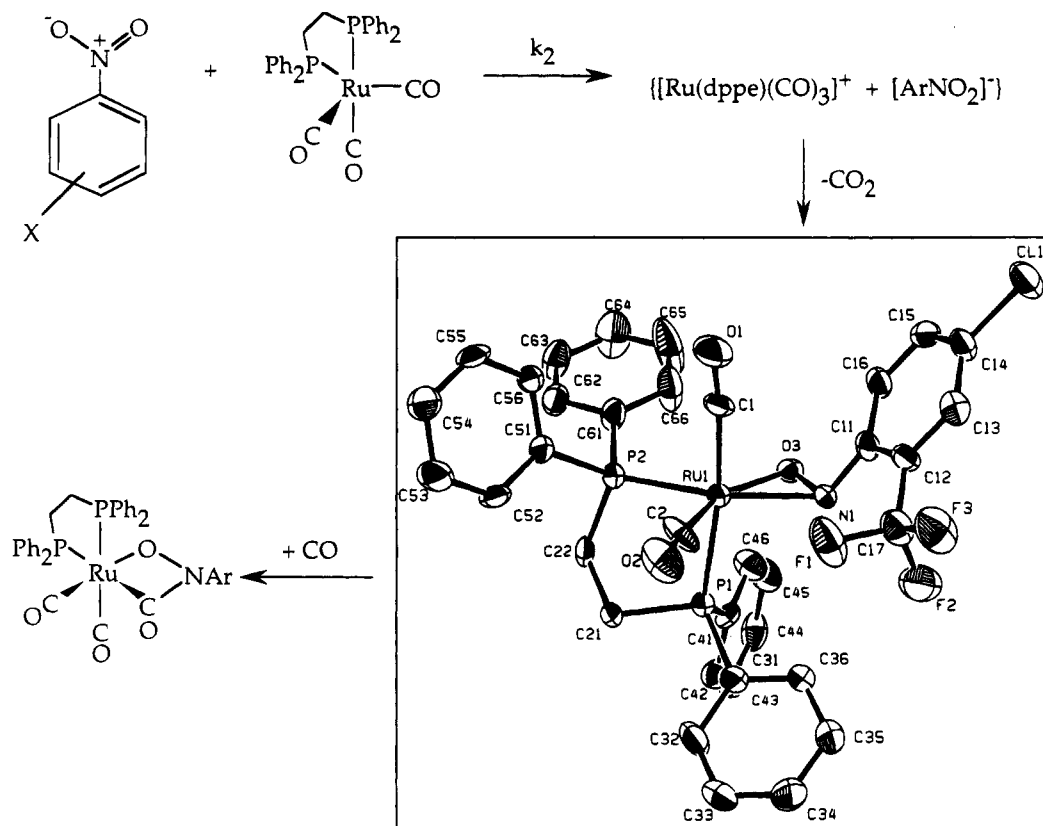
**Figure 1.** Scheme showing the reactions and the ORTEP drawing of Ru(dppe)(CO)$_2$(η^2-ONC$_6$H$_3$ClCF$_3$). Relevent bond distances (Å): Ru1—N1, 2.115(7); Ru1—O3, 2.054(6); Ru1—P1, 2.401(3); Ru1—P2, 2.333(3); Ru1—Cl, 1.918(9); Ru1—C2, 1.88(1). Bond angles (deg): P2—Ru1—N1, 148.0(2); P1—Ru1—Cl, 172.3(3); C2—Ru1—O3, 157.3(4); O3—N1—C11, 112.2(7).

the nitroaromatic, and a crystalline product was ultimately isolated from the reaction between 5-chloro-2-nitrobenzotrifluoride in 68% yield. This reaction was conducted at 0 °C, and the product was isolated as a powder from a concentrated THF solution by the addition of hexane to the reaction mixture at −78 °C. Dark red needles were grown from a CH$_2$Cl$_2$/hexane solution at −25 °C.[23]

A single-crystal X-ray crystallographic analysis[24] established that the structure contained an η^2-ArNO ligand (Figure 1). The geometry around the N atom is pyramidal, and the length of the N—O bond (1.411(9) Å) is slightly shorter than that of the single bond in hydroxylamine (1.46 Å).[25] The N—O bond length is closer to those for the only other structurally characterized monometallic complexes containing η^2-ArNO ligands: oxo(phenylnitroso)(pyridine-2,6-dicarboxylato)-(hexamethylphosphoramide)molybdenum(VI) (1.416(7) Å),[26] bis(triphenylphosphine)(phenylnitroso)platinum-(II) (1.410(7) Å),[27] and (pentamethylcyclopentadienyl)-(phenylimido)(phenylnitroso)phenyltungsten(VI) (1.432-(6) Å).[28] The dihedral angle along Ru1—O3—N1—C11 is 121.7°, and the orientation adopted by the nitro-

soarene ligand minimizes steric interaction between itself and the aromatic rings of the dppe ligand. The similarity of the N—O bond lengths to that in hydroxylamine suggests that the ligand should be considered dianionic and the metal as a d^6 Ru^{2+} complex. The remaining portion of the structure is similar to that of other compounds containing the Ru(dppe)(CO)$_2$ fragment.[11,12]

The rate of the reaction between ArNO$_2$ and Ru(dppe)(CO)$_3$, monitored for at least 4 half-lives, was first order in each reagent and was not inhibited by CO. The presence of isosbestic points in the spectra was consistent with the absence of detectable intermediates between Ru(dppe)(CO)$_3$ and Ru(dppe)(CO)$_2$(η^2-ONAr). A Hammett σ–ϱ plot (Figure 2) was linear for five para substituents ranging from −OMe (σ_p = −0.27) to −CF$_3$ (σ_p = 0.54), and the derived value of ϱ = +3.9 was consistent with a substantial negative charge buildup on the nitroaromatic in the transition state of the rate-determining step. In addition, a plot of the log k_2 vs the $E_{1/2}$ values of the nitroaromatics was linear, which is consistent with, but does not prove, an outer-sphere electron-transfer mechanism. These results parallel those reported by Berman and Kochi[29] in their study of the kinetics of eq 3, which proceeded via an electron-

$$\text{Ni(PR}_3)_4 + \text{ArNO}_2 \rightarrow$$

$$\text{Ni(PR}_3)_2(\text{ArNO}) + \text{PR}_3 + \text{PR}_3\text{O} \quad (3)$$
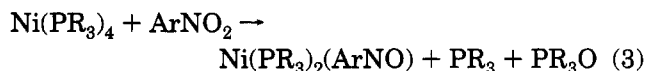
transfer mechanism in the rate-determining step following initial dissociation of one phosphine ligand. The

(24) Crystal data for Ru(dppe)(CO)$_2$(η^2-ONC$_6$H$_3$ClCF$_3$)·CH$_2$Cl$_2$: crystal system monoclinic, space group $P2_1/c$ (No. 14), a = 14.556(8) Å, b = 12.903(6) Å, c = 20.10(1) Å, β = 105.60(6)°, V = 3636(8) Å^3, Z = 4, temperature −100 °C, scan type ω–2θ, refinement method full-matrix least squares, R = 0.065, R_w = 0.068.

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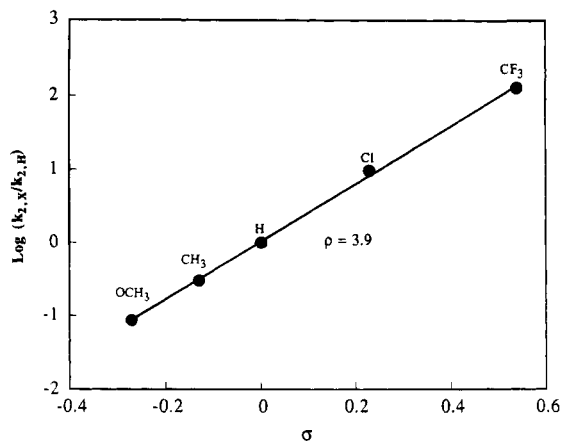(29) Berman, R. S.; Kochi, J. K. *Inorg. Chem.* **1980**, *19*, 248.

Figure 2. Hammett σ–ϱ plot for the reaction between Ru-(dppe)(CO)$_3$ and p-XC$_6$H$_4$NO$_2$. The ordinate is the log of the ratio of k_2 of the para substituent to k_2 of PhNO$_2$.

transition state of the rate-determining step was proposed to involve a direct interaction between the intermediates ArNO$_2^-$ and Ni(PR$_3$)$_3^+$.

The lack of CO inhibition suggests that CO dissociation from Ru(dppe)(CO)$_3$ does not precede the electron-transfer event. The reversible $E_{1/2}$ value for the reduction of nitrobenzene in acetonitrile is -1.14 V vs SCE.[30] Unfortunately, no reversible process was observed for the oxidation of Ru(dppe)(CO)$_3$ using cyclic voltammetry. The appearance of an anodic wave at $+0.171$ V vs Ag/AgCl in CH$_2$Cl$_2$ coupled with the known $E_{1/2}$ value of $+0.200$ V for the closely related complex Ru(PPh$_3$)$_2$-(CO)$_3$ suggested a similar value would be an appropriate estimate for Ru(dppe)(CO)$_3$.[31] The combined values gave a cell potential somewhat greater than 1 V. Strong interactions between the radical cation and anion, including the possible onset of bond formation (C—O or Ru—(ONAr)), could offset the unfavorable cell potential that was calculated on the assumption of no interactions. Because we cannot determine the presence of such interactions or the nature of the possible interactions, the transition state is represented in Figure 1 with a formula only. The formation of an intermediate on the reaction coordinate is reasonable; however, as such species was detected during these studies.

The insertion of CO into the Ru—N bond of Ru(dppe)-(CO)$_2$(η^2-ONAr) was also effected by the substituents

on the aromatic ring; however, the rate was retarded by electron-withdrawing substituents. With a methyl substituent, we previously reported the high-yield preparation of **2** with o-nitrotoluene, a reaction that proceeded with no evidence of an intermediate.[11] We infer that the reaction to produce the intermediate nitrosoarene complex was slow relative to its subsequent reaction with CO. With a trifluoromethyl substituent, the room-temperature reaction of Ru(dppe)(CO)$_2$(η^2-ONC$_6$H$_4$CF$_3$) with CO (2 atm) produces **2** in 33% yield (based on the integration of the ^{31}P NMR spectrum) and a smaller amount of **1**, and the half-life of this transformation is 2 h. As a small amount of aniline was observed by gas chromatography, the source of **1** appears to result from the reaction of Ru(dppe)(CO)$_2$(η^2-ONC$_6$H$_4$CF$_3$) or **2** with adventitious water. The ^{31}P NMR spectrum indicated that the balance of the ruthenium was present as two, as yet unidentified, metal complexes. Finally, the presence of both a chloro and a trifluoromethyl substituent yielded a complex, Ru(dppe)(CO)$_2$[η^2-ONC$_6$H$_3$-Cl(CF$_3$)], that did not react at all with CO at room temperature. If we recall that the η^2-ONAr ligand can be considered as dianionic, the transition state of the insertion of CO into the Ru—N bond becomes higher in energy as the nitrogen loses negative charge.

In conclusion, we have established the importance of electron transfer during the initial substrate—catalyst interaction and first oxygen atom transfer event. In tandem with these kinetic results, isolation and structural characterization of the π-bound nitrosoarene and study of its reaction with CO provide a more complete picture of the first phase in the catalytic carbonylation of nitroaromatics.

Supplementary Material Available: A listing of the kinetic data, a table giving a summary of the crystallographic data, and listings of atomic positions, thermal parameters, and bond distances and angles (15 pages). Ordering information is given on any current masthead page.

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