Oxidative Coupling of Rhodium Phenyl Imido/Amido Complexes[1]

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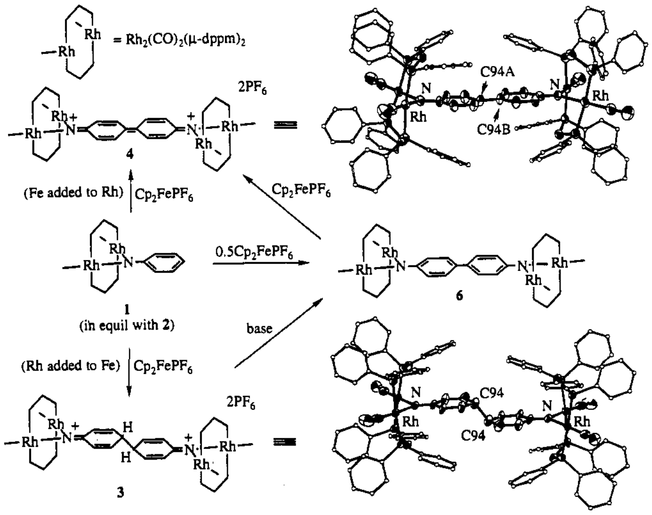
In previous work we found that tautomeric mixtures of the late transition metal imido and amido complexes $Rh_2(\mu\text{-NPh})(CO)_2(\mu\text{-dppm})_2$ (**1**) and $Rh_2(\mu\text{-NHPh})(CO)_2(\mu\text{-dppm})(\mu\text{-dppm-H})$[2] (**2**) (hereafter designated as **1/2**) undergo electrophilic ring addition reactions at the NPh group.[3] A single electron transfer mechanism was considered. Such a mechanism would require oxidation of the imido/amido complex to a radical cation. To establish this possibility, we investigated the oxidation chemistry of this system. We found a rich chemistry consistent with formation and coupling of an amido radical cation. This chemistry, described here, is closely related to the well-studied oxidation chemistry of aniline and its derivatives.[4]

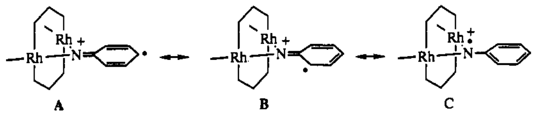
Addition of $Rh_2(\mu\text{-NPh})(CO)_2(\mu\text{-dppm})_2/Rh_2(\mu\text{-NHPh})(CO)_2(\mu\text{-dppm})(\mu\text{-dppm-H})$ (**1/2**)[5] to slightly more than 1 equiv of Cp_2FePF_6 cleanly produces orange $[(\mu\text{-dppm})_2(CO)_2Rh_2(\mu,\mu\text{-}NC_6H_5C_6H_5N)Rh_2(CO)_2(\mu\text{-dppm})_2](PF_6)_2$ (**3**)[6] and Cp_2Fe (Scheme 1). The crystal structure of **3**[7] clearly shows para-coupling of the NPh rings, yielding a linked quinoneimine structure. Consistent with the solid state structure, an upfield shift of the ring protons is observed, indicating a loss of aromaticity.

Different results are obtained when the order of addition is reversed. Thus, addition of 1 equiv of Cp_2FePF_6 to a solution of **1/2** yields $[(\mu\text{-dppm})_2(CO)_2Rh_2(\mu,\mu\text{-}NC_6H_4C_6H_4N)Rh_2(CO)_2(\mu\text{-dppm})_2](PF_6)_2$ (**4**),[8] $[Rh_2(\mu\text{-NHPh})(CO)_2(\mu\text{-dppm})_2]PF_6$ (**5**), and Cp_2Fe (Scheme 1). The crystal structure of **4**,[9] formally the dehydrogenation product of **3**, shows a diphenoquinonediimine structure, now with a C–C double bond joining the rings.

Scheme 1



Scheme 2



Yet another coupled product is obtained when 0.5 equiv of Cp_2FePF_6 is added to **1/2**. The resulting products are $[Rh_2(\mu\text{-NHPh})(CO)_2(\mu\text{-dppm})_2]PF_6$ (**5**) and the benzidine derivative $[(\mu\text{-dppm})_2(CO)_2Rh_2(\mu,\mu\text{-}NC_6H_4C_6H_4N)Rh_2(CO)_2(\mu\text{-dppm})_2]$ (**6**).[10] This same mixture is obtained when **1/2** is added to isolated **3**. Alternatively, **6** is prepared by deprotonation of isolated **3** with $LiN(SiMe_3)_2$. Finally, oxidation of **6** with Cp_2FePF_6 gives **4** (Scheme 1).

These results are best explained by starting with the initial formation of the cation radical **A** (Scheme 2).[11] Radical coupling then yields **3**. Deprotonation of **3** to **6** and oxidation of **6** to **4** explains the different products obtained under the different reaction conditions. Thus, addition of **1/2** to Cp_2FePF_6 generates **3** without any significant amounts of strong basic **1/2** being present in solution, and **3** is the observed final product. With addition of Cp_2FePF_6 to **1/2**, **3** is generated in the presence of **1/2**, which readily deprotonates **3**, giving the mixture of **6** and **5**. The reaction stops here with 0.5 equiv of Cp_2FePF_6, but with 1 equiv, remaining Cp_2FePF_6 oxidizes **6** to **4**.

The proposed radical cation **A** is observable by electrochemical oxidation of **1/2**. A one electron oxidation wave is observed at –0.06 V vs SCE.[12] The oxidation is chemically reversible at fast scan rates but at slower scan rates begins to show chemical irreversibility by intensity loss in the return reduction wave.[13] Other resonance forms **B** and **C** are also possible for the radical cation, but, as in previously observed ring addition reactions of **1/2**,[2] steric factors prevent coupling through these other possible radical sites.

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[1] Part 14 of Late Transition Metal μ-Oxo and μ-Imido Complexes. Part 13: Yang, Y.; Sharp, P. R. *J. Am. Chem. Soc.* **1994**, *116*, 6983–6984.

[2] dppm, bis(diphenylphosphino)methane; dppm-H, bis(diphenylphosphino)methanide.

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[4] Leading references: (a) Seo, E. T.; Nelson, R. F.; Fritsch, J. M.; Marcoux, L. S.; Leedy, D. W.; Adams, R. N. *J. Am. Chem. Soc.* **1966**, *88*, 3498. (b) Yang, H.; Wipf, D. O.; Bard, A. J. *J. Electroanal. Chem.* **1992**, *331*, 913. (c) Yang, H.; Bard, A. J. *J. Electroanal. Chem.* **1992**, *339*, 423. (d) Larumbe, D.; Gallardo, I.; Andieux, C. P. *J. Electroanal. Chem.* **1991**, *304*, 241.

[5] Ge, Y.-W.; Peng, F.; Sharp, P. R. *J. Am. Chem. Soc.* **1990**, *112*, 2632–2640.

[6] Data for **3**: ^{31}P NMR (36 MHz, CD_2Cl_2) δ 21.9 (dm, $J^x_{RhP} = 139.2$ Hz); ^1H NMR (300 MHz, CD_2Cl_2) δ 7.7–7.1 (m, 80H, Ph), 5.70 and 5.54 (d and d, 4H and 4H, $J_{HH} = 9.5$ Hz, NC_6H_5), 3.28 and 3.07 (m and m, 4H and 4H, PCH_2P), 2.45 (br, 2H, NC_6H_5); IR (CH_2Cl_2) 1986 sh, 1975 s cm^{-1}.

[7] Crystals of $\mathbf{3}\cdot 8C_7H_8\cdot 2ClCH_2CH_2Cl$ from toluene/$ClCH_2CH_2Cl$ are monoclinic ($P2_1/n$) with (–100 °C) $a = 18.935(3)$ Å, $b = 25.3870(20)$ Å, $c = 17.0740(2)$ Å, $\beta = 91.965(6)°$, $V = 8202.7(17)$ Å^3, $d_{calc} = 1.40$ g/cm^3, and $Z = 2$; $R = 0.080$, $R_w = 0.136$. Selected distances (Å): Rh1–N 2.034(7), Rh2–N 2.032(7), N–C91 1.303(10), C91–C92 1.445(13), C91–C96 1.439(13), C92–C93 1.336(12), C93–C94 1.505(14), C94–C95 1.478(14), C95–C96 1.393(14), C94–C94a 1.569(18).

[8] Data for **4**: ^{31}P NMR (36 MHz, CH_2Cl_2) δ 22.3 (dm, $J^x_{RhP} = 138$ Hz); ^1H NMR (300 MHz, CD_2Cl_2) δ 7.8–6.9 (m, 80H, Ph), 6.68 and 5.96 (d and d, 4H and 4H, $J_{HH} = 10$ Hz, NC_6H_4), 3.07 (m, 8H, PCH_2P); IR (CH_2Cl_2) 1984 sh, 1975 s cm^{-1}.

[9] Crystals of $\mathbf{4}\cdot 3CH_2Cl_2\cdot 2.5Et_2O$ from CH_2Cl_2/ether are monoclinic ($P2_1/n$) with (22 °C) $a = 27.873(3)$ Å, $b = 17.4520(9)$ Å, $c = 26.607(3)$ Å, $\beta = 96.706(4)°$, $V = 12\,854.1(22)$ Å^3, $d_{calc} = 1.54$ g/cm^3, and $Z = 4$; $R = 0.053$, $R_w = 0.075$. Selected distances (Å): Rh1A–NA 2.047(7), Rh1B–NB 2.038(6), Rh2A–NA 2.042(7), Rh2B–NB 2.038(7), C91A–C92A 1.410(12), C91A–C96A 1.452(12), C91B–C92B 1.443(12), C91B–C96B 1.451(12), C92A–C93A 1.365(12), C92B–C93B 1.346(12), C93A–C94A 1.424(12), C93B–C94B 1.429(12), C94A–C94B 1.402(11), C94A–C95A 1.438(12), C94B–C95B 1.439(13), C95A–C96A 1.317(12), C95B–C96B 1.364(12).

[10] Data for **6**: (as with related imido complexes (ref 5), **6** appears to be in rapid equilibrium with its amido tautomer at ambient temperatures) ^{31}P NMR (202 MHz, CD_2Cl_2, 22 °C) δ 20 (br, unresolved) (at –48 °C, the spectrum resolves to a symmetric peak at δ 21.7 (dm, $J^x_{RhP} = 139.2$ Hz) assigned to the imido tautomer; other small peaks were present, but these could not be positively assigned to the amido tautomer; IR data suggest that one tautomer dominates); ^1H NMR (300 MHz, CD_2Cl_2, 22 °C) δ 7.8–6.9 (m, 88H, Ph and NC_6H_4), 3.70 and 3.30 (m and m, 4H and 4H, PCH_2P); IR (CH_2Cl_2) 1973 sh, 1964 s cm^{-1}.

[11] It seems unlikely that the amido tautomer is involved in the oxidation, as electron density in the ring of the amido tautomer is very much less than that of the imido tautomer.

[12] Au disc electrode, NBu_4PF_6/CH_2Cl_2, internal Cp_2Fe reference corrected to the SCE.

[13] Similar results are reported for the oxidation of tertiary arylamines, where the radical cations are detected electrochemically and by optical and EPR spectroscopy (see ref 4).

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The above results demonstrate a new type of reactivity for arylimido complexes. The facile formation of the relatively stable imido radical and the following chemistry suggest that the imido complex is like a very electron rich aniline derivative. Related oxidative coupling reactions should be possible in other systems where electron pair donation into the ring is present and where steric factors prevent reactions at the heteroatom centers. Such coupling reactions have been observed for Pt arylamido complexes,[14] and a Mn arylamido radical has been isolated.[15] Such reactivity may also be possible for aryloxo complexes and would be related to the metal-catalyzed oxidative coupling of phenol to diphenoquinones.[16]

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Supplementary Material Available: Experimental procedures, crystal structure reports, positional and thermal parameters and bond distances and angles for **3** and **4** (24 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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