

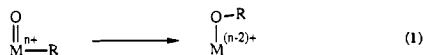
## Formation of Rhenium Phenoxides from Arenes via C–H Activation and Aryl-to-Oxo Migration

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The migration of a transition-metal alkyl or aryl ligand to a terminal oxo group (eq 1) has been proposed as a mechanism for oxidizing these organic fragments.<sup>3</sup> Migrations of this sort,



however, have never been directly observed,<sup>4,5</sup> though the reverse reaction, involving alkyl or hydride migration from oxo- to a metal center, has been documented in a handful of cases.<sup>6</sup> Here we report the direct observation of photochemical rearrangement of rhenium oxo-aryl complexes to rhenium phenoxide complexes by an intramolecular [1,2]-shift. The oxo-aryl complexes are prepared by C–H activation of arenes by rhenium oxo compounds, so one-pot transformation of arenes to phenoxides can be achieved. A rhenium oxo-ethyl complex also undergoes net photochemical rearrangement, but by a different mechanism involving rhenium-carbon bond homolysis.

The rhenium(V) oxo iodide complex (HBpz<sub>3</sub>)ReO(Cl)I (**1**)<sup>7</sup> (HBpz<sub>3</sub> = hydridotris(1-pyrazolyl)borate), available from the

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(2) Presidential Young Investigator, 1988–1993.

(3) Sharpless, K. B.; Teranishi, A. Y.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1977**, *99*, 3120. Hentges, S. G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 4263. Göbel, T.; Sharpless, K. B. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1329.








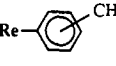

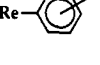
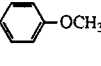
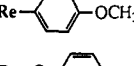
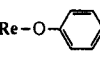
(4) This or similar migrations have been proposed on the basis of indirect evidence, e.g.: Reichle, W. T.; Carrick, W. L. *J. Organomet. Chem.* **1970**, *24*, 419. Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 1759. Vivanco, M.; Ruiz, J.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1993**, *12*, 1802.

(5) Transition-metal alkyls have been converted to alkoxides using external oxidants such as N<sub>2</sub>O and peroxides: Parkin, G.; Bercaw, J. E. *J. Am. Chem. Soc.* **1989**, *111*, 391. Matsunaga, P. T.; Hillhouse, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 2075–2077 and references therein.

(6) (a) van Asselt, A.; Burger, B. J.; Gibson, V. C.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 5347. (b) Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21. (c) Parkin, G.; van Asselt, A.; Leahy, D. J.; Whinnery, L.; Hua, N. G.; Quan, R. W.; Henling, L. M.; Schaefer, W. P.; Santarsiero, B. D.; Bercaw, J. E. *Inorg. Chem.* **1992**, *31*, 82–85. (d) Nelson, J. E.; Parkin, G.; Bercaw, J. E. *Organometallics* **1992**, *11*, 2181–2189. (e) Tahmassebi, S. K.; Conry, R. R.; Mayer, J. M. *J. Am. Chem. Soc.* **1993**, *115*, 7553–4.

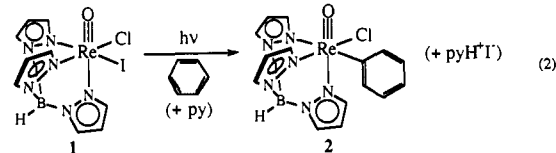
(7) Partial spectroscopic data for selected new compounds follow. For more complete data, see the supplementary material. Unassigned peaks in the <sup>1</sup>H NMR are due to the pyrazoles and have *J* = 2 Hz. For **1**: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 5.95, 6.57, 6.59 (t, 1 H), 7.40, 7.49, 7.93, 7.96, 8.19, 8.58 (d, 1 H); IR 2518 (ν<sub>BH</sub>), 977 (ν<sub>ReO</sub>); FABMS 578 (M + H). **2**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 5.16, 5.64, 5.76 (t, 1 H), 6.69, 6.95, 7.07, 7.12, 7.23, 8.39 (d, 1H), 7.02 (t, *J* = 8 Hz, 1 H; para), 7.45 (t, *J* = 8 Hz, 2 H; meta), 7.76 (d, *J* = 8 Hz, 2 H; ortho); IR 2520 (ν<sub>BH</sub>), 978 (ν<sub>ReO</sub>); MS 528 (M<sup>+</sup>). **3**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 2.22, 8.74, 13.30 (t, 1 H, pz), -27.40, -17.48, -10.89, -6.12, -4.07, 5.22 (d, 1 H, pz), -2.32 (br d, *J* = 4 Hz, 2 H; py 2,6-H), -0.79 (t, *J* = 8 Hz, 1 H; py 4-H), 16.92 (dd, *J* = 8, 6 Hz, 2 H; py 3,5-H); -11.71 (d, *J* = 8 Hz, 2 H; OPh ortho), -4.73 (t, *J* = 8 Hz, 1 H; OPh para), 10.56 (t, *J* = 8 Hz, 2 H; OPh meta); IR 2508 (ν<sub>BH</sub>), 1584 (ν<sub>C=C</sub>), 1258 (ν<sub>C=O</sub>); MS 607 (M<sup>+</sup>). **6**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 2.45 (t, *J* = 8 Hz, 3 H; Re-CH<sub>2</sub>CH<sub>3</sub>); 6.06, 7.81 (dq, *J* = 13, 8 Hz, 1 H each; Re-CHHCH<sub>3</sub>); 5.30, 5.69, 5.77 (t, 1 H, pz), 6.70, 7.08, 7.10, 7.23, 7.55, 8.35 (d, 1 H, pz); IR 2518 (ν<sub>BH</sub>), 980 (ν<sub>ReO</sub>); FABMS 480 (M<sup>+</sup>). **7**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 2.39, 10.22, 13.44 (t, 1 H, pz), -28.88, -14.89, -7.10, -3.50, -1.82, +5.71 (d, 1 H, pz), -0.01 (d, *J* = 5 Hz, 2 H; py 2,6-H), +0.82 (t, *J* = 7 Hz, 1 H; py 4-H), 16.35 (t, *J* = 7 Hz, 2 H; py 3,5-H), -10.00 (t, *J* = 7 Hz, 3 H; -OCH<sub>2</sub>CH<sub>3</sub>), +76.94 (m, 2 H; -OCHHCH<sub>3</sub>); irradiating the triplet at δ = -10.0 collapses the multiplet to an AB pattern with *J*<sub>AB</sub> = 12 Hz and Δδ<sub>AB</sub> = 0.03 ppm; IR 2506 (ν<sub>BH</sub>), 1275, 1262 (ν<sub>C=O</sub>); FABMS 559 (M<sup>+</sup>).

**Table 1.** Yields for Photochemical Arene Activation by (HBpz<sub>3</sub>)ReO(Cl)I (**1**)<sup>a</sup>

Solvent	Products <sup>b</sup>	Yield <sup>a</sup> without py	Yield <sup>a</sup> py added
	Re- 	35%	90%
	Re- 	c	72%
	Re- 	c	46%
	Re- 	37% <i>m:p</i> = 16:84	79% <i>m:p</i> = 13:87
	Re- 	32% <i>o:m:p</i> = 43:2:56	88% <i>o:m:p</i> = 41:2:56
	Re- 	24%	47%
	Re-O- 	42%	44%

<sup>a</sup> Reactions were performed at approximately 5 mM **1** in arene solvent (with addition of 12 equiv of pyridine where indicated) and were irradiated for about 3 days by an Oriol 200-W Hg/Xe lamp with a 455-nm long-pass filter. Yields were determined by integration of <sup>1</sup>H NMR spectra against added Me<sub>4</sub>Si or (Me<sub>3</sub>Si)<sub>2</sub>O and are reported relative to the amount of rhenium consumed in the reactions. <sup>b</sup> Re = (HBpz<sub>3</sub>)Re(O)Cl. <sup>c</sup> Not examined.

known dichloride complex (HBpz<sub>3</sub>)ReOCl<sub>2</sub>,<sup>8</sup> reacts with benzene under photochemical conditions to form air- and water-stable (HBpz<sub>3</sub>)ReO(Ph)Cl (**2**, eq 2),<sup>7</sup> in which the iodide ligand is replaced by a phenyl group. Yields of **2** of 30–40% are achieved



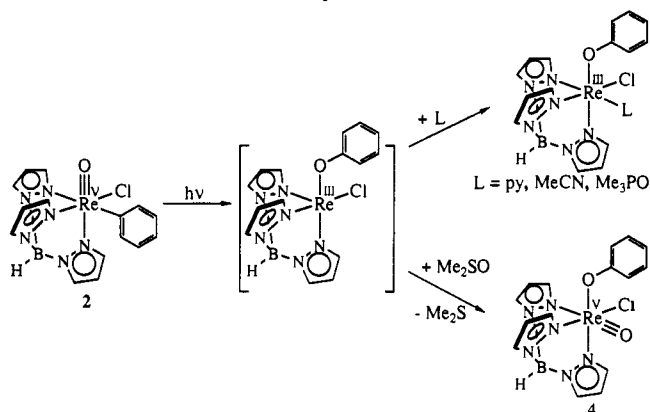
after a day of photolysis through a Pyrex filter or several days through a 455-nm filter. If a few equivalents of pyridine are added to the solution, the yield of **2** from **1** increases dramatically, to 90% by NMR, and pyridinium iodide precipitates from the solution (eq 2). The increased yield in the presence of pyridine does not appear to derive from its scavenging of HI, since more hindered bases such as triethylamine or 2,6-lutidine do not affect the yield.

The diiodide complex (HBpz<sub>3</sub>)ReOI<sub>2</sub> reacts similarly on photolysis in benzene, forming a mixture of (HBpz<sub>3</sub>)ReO(Ph)I and (HBpz<sub>3</sub>)ReO(Ph)<sub>2</sub>. The structure of the latter compound has been confirmed by X-ray crystallography.<sup>9</sup> At least one iodide

(8) (a) Abrams, M. J.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1984**, *82*, 125. (b) Degnan, I. A.; Behm, J.; Cook, M. R.; Herrmann, W. A. *Inorg. Chem.* **1991**, *30*, 2165. (c) Brown, S. N.; Mayer, J. M. *Inorg. Chem.* **1992**, *31*, 4091–4100.

(9) Crystallographic data will be reported in a future publication.

## Scheme 1. Photochemical Aryl-to-Oxo Rearrangements

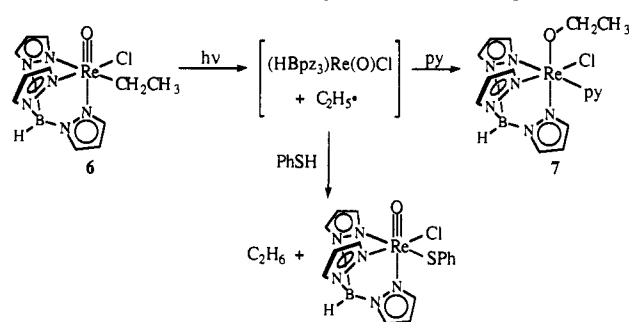


ligand appears to be needed for arylation, as (HBpz<sub>3</sub>)ReOCl<sub>2</sub> is unreactive. The scope and selectivity of the photochemical reaction of **1** with arenes are illustrated by the results listed in Table 1. Reactions with methyl-substituted arenes yield only aryl products, not benzylic ones, even with the rather hindered mesitylene. The regioselectivity of activation of toluene, fluorobenzene, and anisole indicates that the reaction proceeds with modest electrophilic selectivity, which is unaffected by the presence of pyridine.

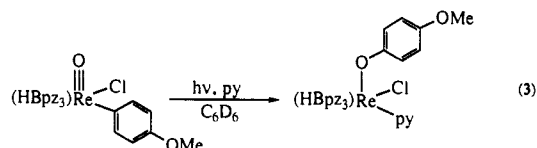
UV photolysis of solutions containing pyridine and the rhenium(V) oxo-phenyl complex (HBpz<sub>3</sub>)ReO(Ph)Cl (**2**) causes phenyl-to-oxo migration, forming the rhenium(III) phenoxide complex (HBpz<sub>3</sub>)Re(OPh)(Cl)(py) (**3**). The conversion is slow (~80% complete in 10 days) but proceeds in good yield (85% yield based on reacted **2**). Prolonged photolysis of **1** in the presence of pyridine gives **3** without isolation of the intermediate **2**, effecting a one-pot conversion of benzene to a rhenium phenoxide. The assignment of the structure of red, paramagnetic **3** is based on spectroscopic<sup>7</sup> and analytical data, an X-ray structure determination,<sup>9</sup> and its independent synthesis from (HBpz<sub>3</sub>)ReO(OPh)(Cl) (**4**) and P(OMe)<sub>3</sub> in the presence of pyridine (32% yield). The phenoxide group may be removed from the rhenium by treatment of **3** with Me<sub>3</sub>SiCl or HCl, which release Me<sub>3</sub>SiOPh or phenol, respectively, and form (HBpz<sub>3</sub>)ReCl<sub>2</sub>(py). Photolysis of **2** in the presence of acetonitrile or Me<sub>3</sub>PO also produces rhenium(III) phenoxide adducts (Scheme 1). When Me<sub>2</sub>SO is present, oxygen atom transfer to rhenium(III) occurs to give the oxo-phenoxide complex **4**.

Phenyl-to-oxygen migration is predominantly intramolecular, as the products of photolysis of a mixture of (HBpz<sub>3</sub>)Re(<sup>18</sup>O)(C<sub>6</sub>H<sub>5</sub>)(Cl) and (HBpz<sub>3</sub>)Re(<sup>16</sup>O)(C<sub>6</sub>D<sub>5</sub>)(Cl) show little crossover (<15%) by FABMS. This rules out the intermediacy of free phenyl radical in the rearrangement. Consistent with this, photolysis of **2** in neat CD<sub>3</sub>CN proceeds smoothly to give (HBpz<sub>3</sub>)Re(OPh)(Cl)(NCCD<sub>3</sub>) (**5**), with no formation of C<sub>6</sub>H<sub>5</sub>D, and addition of the radical trap thiophenol does not impede rearrangement in benzene/pyridine.<sup>10</sup> The intramolecularity of the reaction and the insensitivity of its apparent rate to added ligands (py, MeCN, Me<sub>3</sub>PO, Me<sub>2</sub>SO) indicate that rearrangement takes place directly to form the five-coordinate rhenium(III) complex [(HBpz<sub>3</sub>)Re(OPh)(Cl)] (Scheme 1). The ipso carbon of the phenyl group becomes bound to oxygen, since the *p*-anisyl complex (HBpz<sub>3</sub>)ReO(C<sub>6</sub>H<sub>4</sub>OMe)(Cl) gives exclusively the *p*-methoxyphenoxide complex (HBpz<sub>3</sub>)Re(OC<sub>6</sub>H<sub>4</sub>OMe)(py)(Cl) on photolysis in the presence of pyridine (eq 3). Thus, photochemical

## Scheme 2. Photochemical Alkyl-to-Oxo Rearrangements

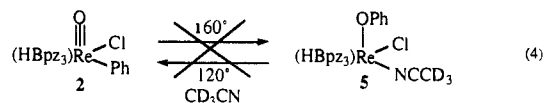


metal-to-oxo migration of aryl groups in this system appears to take place by a direct, intramolecular [1,2]-aryl shift.



Alkyl groups can also migrate under photochemical conditions. Photolysis of the oxo-ethyl complex (HBpz<sub>3</sub>)ReO(C<sub>2</sub>H<sub>5</sub>)Cl (**6**)<sup>7</sup> in benzene in the presence of pyridine produces a rhenium(III) alkoxide (HBpz<sub>3</sub>)Re(OC<sub>2</sub>H<sub>5</sub>)(Cl)(py) (**7**),<sup>7</sup> similar to the phenoxide complexes noted above (Scheme 2). This photolysis is complete in a day, much faster than that of **2**, but the yield of alkoxide product is much lower (45%). Ethane and ethylene are also observed on photolysis of **6**, suggesting that ethyl radicals are being produced. In fact, these radicals are intimately involved in the migration, since addition of radical traps such as oxygen or thiophenol completely suppresses rearrangement. In the presence of thiophenol, ethane and the rhenium(V) thiophenoxide complex (HBpz<sub>3</sub>)ReO(SPh)(Cl)<sup>8b</sup> are formed (Scheme 2). Thus, in contrast to the aryl migration, photochemical migration of the saturated ethyl ligand occurs by initial homolysis of the rhenium-carbon bond and involves free ethyl radical as an intermediate.

The rearrangements observed are exclusively photochemical; no thermal migrations are seen. For example, heating **2** for a month in CD<sub>3</sub>CN at 160 °C causes less than 10% decomposition with no sign of rearrangement. Its rearrangement product, **5**, decays over several days at 120 °C to form an unidentified diamagnetic product and some free phenol, but no **2** (eq 4). There



is thus a high kinetic barrier to thermal rearrangement in this system ( $\Delta G^\ddagger > 40$  kcal/mol for **2**  $\rightarrow$  **5**,  $\Delta G^\ddagger > 32$  kcal/mol for **5**  $\rightarrow$  **2**). Likewise, neither the ethyl complex **6** nor the ethoxide complex **7** rearranges over several days at 110 °C. Work is in progress to find systems in which thermal, rather than photochemical, alkyl-to-oxo migrations occur.

**Acknowledgment.** We thank the National Science Foundation for generous financial support.

**Supplementary Material Available:** Synthetic, spectroscopic, and analytical data for new compounds (10 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.

(10) Ph<sup>\*</sup> is trapped by CH<sub>3</sub>CN and PhSH at rates of 10<sup>5</sup> M<sup>-1</sup> s<sup>-1</sup> and 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>, respectively: Asmus, K.-D.; Bonifacio, M. In *Radical Reaction Rates in Liquids*; Fischer, H., Ed.; Landolt-Börnstein New Series; Springer-Verlag: Berlin, 1984; Vol. 13, Subvol. b, Carbon-centered Radicals II, pp 26, 182, 193.