Organometallics **1998,** *17,* 3364−3374

On the Mechanism of C−H Bond Activation in the Photochemical Arylation of Rhenium(V) Oxo Iodide Complexes

Seth N. Brown,*[,1] Andrew W. Myers,[2] J. Robin Fulton,[3] and James M. Mayer*

Department of Chemistry, Box 351700, University of Washington,
Seattle, Washington 98195-1700

Received March 23, 1998

Photolysis of the Re(V) oxo−iodide compound ($(HBpz_3)ReO(I)Cl$) (**1**) in arene solvents gives the aryl complexes $(HBpz_3)ReO(Ar)Cl$. Substituted arenes react with electrophilic selectivity exclusively at aromatic C−H bonds, and a variety of functional groups are tolerated. Yields are improved when photolysis is carried out in the presence of pyridine. Photolysis of the diiodide complex, $(HBpz_3)ReOI_2$ (**2**), gives a mixture of mono- and disubstituted Re−aryl complexes, and the diphenyl derivative $(HBpz_3)ReOPh_2$ has been structurally characterized. The isotope effect found when **1** is photolyzed with a 1:1 mixture of C_6H_6 and C_6D_6 was found to depend on the concentration of **1**. Lower concentrations (∼0.5 mM) show a 1.2(2):1 ratio of d_0 to d_5 products, while higher concentrations (∼20 mM) show higher d_0:d_5 ratios of 1.8(2):1. The apparent isotope effects increase with increasing conversion and are also affected by the presence of additives such as pyridine or iodine. Photolysis of **1** with 1,3,5-trideuteriobenzene shows a 4.0(4):1 ratio of C−H vs C−D activation, which is independent of reaction conditions. A mechanism for arene activation is proposed that involves initial arene binding, which discriminates intermolecularly between arenes with a low isotope effect, followed by C−H bond cleavage, which discriminates intramolecularly within an arene with a higher isotope effect. The reactive species appears to be a rhenium(IV) oxo complex which can add aromatic C−H bonds across the Re═O linkage.

Introduction

The activation and functionalization of hydrocarbons has been a major goal of modern organometallic chemistry.[4] Substantial progress has been made in developing and understanding certain systems that form metal−carbon bonds from hydrocarbons. Examples include electron-rich complexes of the later transition metals that undergo intermolecular oxidative-addition reactions with hydrocarbon C−H bonds,[5] electrophilic complexes that form metal−carbon bonds by σ-bond metathesis reactions,[6] and early-transition-metal complexes with metal−nitrogen multiple bonds that undergo addition of C−H bonds across the M−N π bond.[7]

In this paper, we describe the photochemical reactions of rhenium(V) oxo−iodide complexes with arenes, which lead to products in which the iodide ligand has been replaced with an aryl group. This is, to our knowledge, the first example of formation of an isolable oxo−alkyl or −aryl complex from a metal oxo complex and a hydrocarbon. The reaction takes place with considerable selectivity, with rhenium attaching preferentially to more electron-rich sites on aromatic substrates. The presence of both the oxo ligand and the σ-bonded aryl group in the product of the reaction is exciting because the oxo group offers the potential for further reaction—in particular, oxidation—of the organic moiety. This potential has been realized in both photochemical[8] and thermal[9] reactions, establishing tris(pyrazolyl)borate rhenium oxo complexes as capable of both activating and functionalizing aromatic compounds. Preliminary results have been reported.[10]

---

[1] Current address: University of Notre Dame, Department of Chemistry and Biochemistry, 251 Nieuwland Science Hall, Notre Dame, IN 46556-5670. E-mail: Seth.N.Brown.114@nd.edu.

[2] Current address: Union Carbide Corp., 3333 Hwy. 6 S., Houston, TX 77082. E-mail: myersaw@ucarb.com.

[3] Current address: Department of Chemistry, University of California, Berkeley, CA 94720.

[4] *Activation and Functionalization of Alkanes*; Hill, C. L., Ed.; Wiley-Interscience: New York, 1989. *Selective Hydrocarbon Activation, Principles and Progress*; Davies, J. A., Watson, P. L., Liebman, J. F., Greenberg, A., Eds.; VCH: New York, 1990. Crabtree, R. H. *Chem. Rev.* **1995**, *95*, 987−1007. Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154−162. See also refs 5−7.

[5] (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929−3939. (b) Graham, W. A. G. *J. Organomet. Chem.* **1986**, *300*, 81−91. (c) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91−100. (d) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814. (e) Holtkamp, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 848 and references therein. (f) Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1997**, *119*, 10235−10236.

[6] Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51−56. Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schafer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203−219.

[7] (a) Schaller, C. P.; Cummins, C. C.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1996**, *118*, 591−611. Bennett, J. L.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1997**, *119*, 10696−10719 and references therein. (b) Lee, S. Y.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 5877−8 and references therein. (c) de With, J.; Horton, A. D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 903. (d) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729−8731. (e) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1993**, *12*, 3705−3723.

[8] Brown, S. N.; Mayer, J. M. *Organometallics* **1995**, *14*, 2951−2960.

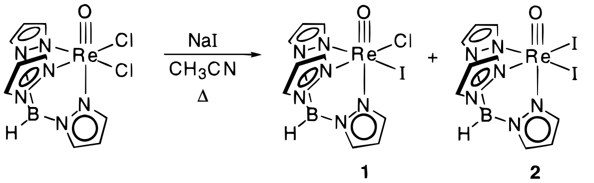
[9] Brown, S. N.; Mayer, J. M. *J. Am. Chem. Soc.* **1996**, *118*, 12119−12233.

[10] Brown, S. N.; Mayer, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 2219−2220.

S0276-7333(98)00216-7 CCC: $15.00

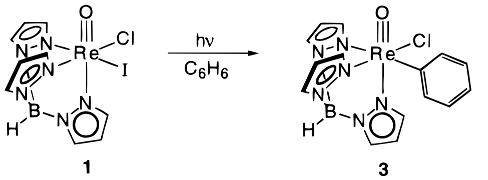
Results

Benzene Activation by Rhenium Iodide Complexes. Tris(pyrazolyl)borate rhenium(V) oxo iodide complexes may be synthesized from the dichloride complex (HBpz$_3$)ReOCl$_2$[11] by treatment with sodium iodide in refluxing acetonitrile (eq 1). The rather vigorous conditions required by this inorganic analogue of the Finkelstein reaction[12] attest to the kinetic inertness of the rhenium−chloride bonds in the starting material. The two products, the green monoiodide complex (HBpz$_3$)ReO(Cl)I (**1**) and the yellow diiodide complex (HBpz$_3$)ReOI$_2$ (**2**), can be separated from each other and the starting materials by chromatography on silica gel. Complex **1** is only available in about 25% yield by this method, however, so a more practical synthesis was developed by treating (HBpz$_3$)ReOCl$_2$ with 1 equiv of silver trifluoromethanesulfonate (silver triflate, AgOTf). Quenching the resulting mixture of rhenium triflate complexes[13] with NaI gives **1** in about 50% yield after chromatographic purification.

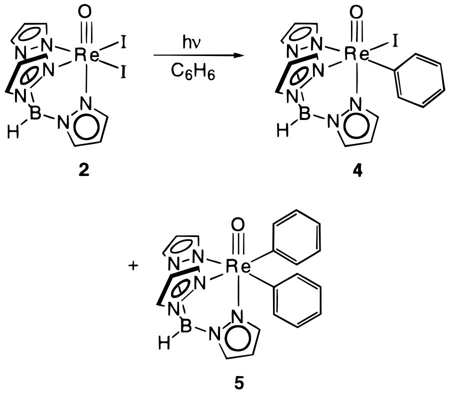


(1)

Photolysis of **1** and **2** in benzene causes the iodide ligands to be replaced by σ-bonded phenyl groups (eqs 2 and 3). At least one iodide ligand appears to be necessary for arylation to take place, as (HBpz$_3$)ReOCl$_2$ is photochemically inert. Irradiation through a filter that blocks radiation with $\lambda < 455$ nm substantially reduces the reaction rate relative to that observed on irradiation through Pyrex (blocking $\lambda < 300$ nm). Irradiation into the d−d band at ca. 700 nm is, therefore, not effective, with irradiation into absorbances in **1** and **2** in the 300−500 nm range being required.



(2)



(3)

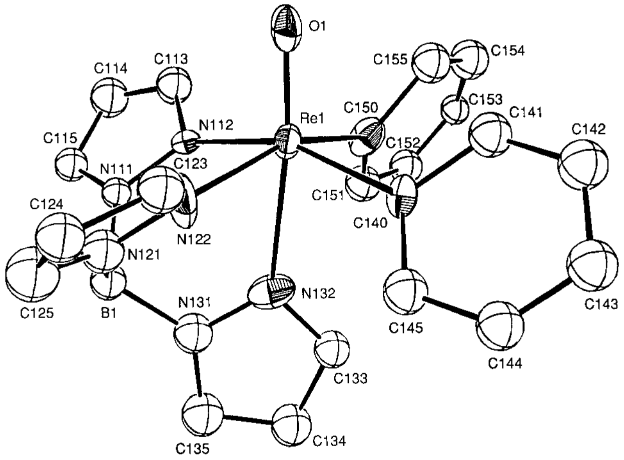


Figure 1. ORTEP drawing of (HBpz$_3$)ReO(Ph)$_2$ (**5**).

Table 1. Crystal Data for (HBpz$_3$)ReO(Ph)$_2$

formula	$C_{21}H_{20}BN_6ORe$
fw	569.44
cryst size, mm	0.10 × 0.10 × 0.10
space group	$P2_1/c$
λ, Å	Mo Kα, 0.710 73
T, °C	25
cell params	
a, Å	15.884(2)
b, Å	17.193(4)
c, Å	17.245(3)
α, deg	90.0
β, deg	116.11(1)
γ, deg	90.0
Z	8
V, Å^3	4227(3)
ρ_{calc}, g cm^{-3}	1.789
decay correction	1.3%
μ, cm^{-1}	58.50
transm coeff	0.853−0.998 (average = 0.943)
no. of reflns measd	8595
no. of unique reflns	6783
no. of obsd reflns ($I > 2.5\sigma I$)	3164
no. of refined params	311
R_{ave}	0.047
R	0.073
R_w	0.073
goodness of fit	1.340

Reactions 2 and 3 suggest that the process occurs one iodide at a time, and indeed, photolysis of purified (HBpz$_3$)ReO(Ph)I (**4**) in benzene gives (HBpz$_3$)ReO(Ph)$_2$ (**5**). Yields of the aryl products on photolysis of (HBpz$_3$)ReO(X)I are low (13% for each product where X = I, 35% for X = Cl, 56% for X = Ph). However, these yields increase dramatically when the reactions are conducted in the presence of pyridine. For example, **3** is formed in 90% yield when **1** is photolyzed in benzene with ∼10 equiv of pyridine. Under these conditions, pyridinium iodide precipitates from solution and can be isolated by filtration in 78% yield, thus accounting for the elements of hydrogen iodide which are lost in the reaction. Scavenging of HI cannot be responsible for the improved yields though, since noncoordinating bases such as triethylamine or 2,6-lutidine have no effect on the yield of arylated product.

Three lines of evidence confirm the formation of rhenium−carbon bonds in the products of these photochemical reactions. First, spectroscopic data and el-

---

[11] (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.

[12] Finkelstein, H. *Chem. Ber.* **1910**, *43*, 1528−1532.

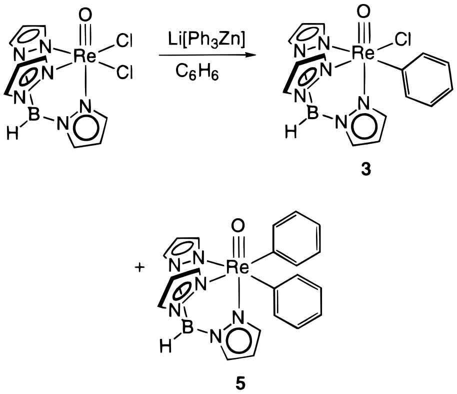
[13] (HBpz$_3$)ReO(OTf)Cl is available in pure form from **1** + AgOTf. DuMez, D. D.; Mayer, J. M. *Inorg. Chem.* **1998**, *37*, 445−453.

Table 2. Selected Bond Distances (Å) and Angles (deg) in $(HBpz_3)ReO(Ph)_2$[a]

Re(1)−O(1)	1.610 (17), 1.648 (14)	Re(1)−N(112)	2.174 (19), 2.157 (20)
Re(1)−C(140)	2.100 (25), 2.065 (24)	Re(1)−N(122)	2.128 (20), 2.130 (19)
Re(1)−C(150)	2.098 (25), 2.093 (21)	Re(1)−N(132)	2.296 (21), 2.266 (20)
O(1)−Re(1)−N(112)	101.7 (7), 96.7 (7)	N(112)−Re(1)−N(122)	87.3 (8), 87.7 (8)
O(1)−Re(1)−N(122)	97.7 (8), 96.3 (7)	N(112)−Re(1)−N(132)	75.4 (7), 79.9 (7)
O(1)−Re(1)−N(132)	172.6 (8), 173.9 (7)	N(112)−Re(1)−C(140)	159.1 (8), 164.5 (8)
O(1)−Re(1)−C(140)	99.2 (9), 98.9 (8)	N(112)−Re(1)−C(150)	84.5 (9), 88.4 (8)
O(1)−Re(1)−C(150)	102.9 (9), 101.2 (8)	N(122)−Re(1)−N(132)	75.5 (9), 78.6 (7)
N(132)−Re(1)−C(140)	83.8 (9), 84.6 (8)	N(122)−Re(1)−C(140)	89.1 (9), 90.0 (8)
N(132)−Re(1)−C(150)	83.6 (9), 83.9 (8)	N(122)−Re(1)−C(150)	158.9 (10), 162.4 (8)
C(140)−Re(1)−C(150)	91.6 (9), 89.2 (9)		

[a] Values for the equivalent bond length or angle in the other crystallographically independent molecule are given after a comma.

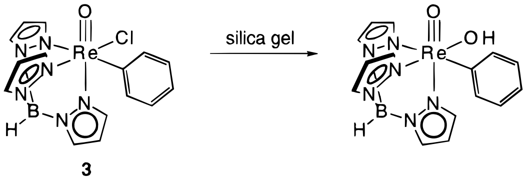
emental analyses are consistent with the formulations of the three oxo−phenyl complexes. Mass spectroscopy indicates their molecular weights and that they are monomeric. IR spectroscopy shows that the complexes retain strong rhenium−oxygen multiple bonds (e.g., ν_{ReO} = 978 cm^{-1} for **3**). NMR spectroscopy indicates that the complexes are diamagnetic, as expected for octahedral d^2 oxo complexes. Second, the diphenyl complex **5** and the phenyl chloride complex **3** can be prepared from $(HBpz_3)ReOCl_2$ by an alternate synthesis using organozinc reagents (eq 4).[9] Finally, the molecular structure of **5** has been ascertained by single-crystal X-ray crystallography.



(4)

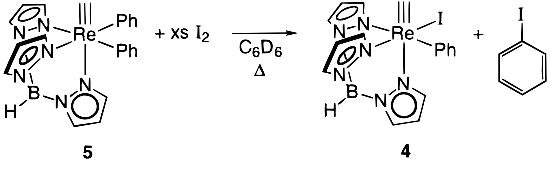
$(HBpz_3)ReO(Ph)_2$ (**5**) crystallizes with two independent molecules of the rhenium complex in the asymmetric unit; an ORTEP diagram of one of the molecules is shown in Figure 1. Crystallographic details are summarized in Table 1, and selected bond lengths and angles are given in Table 2. The two crystallographically independent molecules do not differ significantly from each other. Due to the small crystal size, relatively few reflections were observed, and thus the uncertainties in bond distances and angles are large. The metal−oxo distances (1.629 Å average) are on the extreme short end of those observed for rhenium,[14] which is consistent with the unusually high frequency of the rhenium−oxo stretch of this complex (1002 cm^{-1}; other tris(pyrazolyl)borate oxo−aryl complexes have oxo stretches in the range 978−981 cm^{-1}). The coordination geometry is an octahedron that is distorted, as is typical, by the strong trans influence of the oxo ligand. The phenyl groups are canted so as to lie in the clefts between the cis pyrazoles, probably for steric reasons. This is almost certainly the conformation of the complex in solution, though rotation of the unsubstituted phenyl group is rapid on the NMR time scale.

Reactivity of Rhenium Oxo−Phenyl Complexes. The oxo−aryl complexes **3**−**5** are stable indefinitely when exposed to the atmosphere, whether in solution or in the solid state. They are also thermally robust. For example, **3** may be heated at 160 °C for a month in acetonitrile with less than 10% decomposition, and **5** persists in benzene at 130 °C for at least several days. The complexes may all be purified by flash chromatography on short silica gel columns, although significant losses occur due to reaction with the column. For the phenyl chloride complex at least, some of the lost material may be eluted off the column by ethyl acetate as a violet band. The violet compound is identified as the hydrolysis product (HBpz$_3$)ReO(Ph)(OH) (eq 5) on the basis of its spectroscopic features (a parent ion *m*/*z* = 510 in the mass spectrum, δ Re−O*H* = 13.56 in the ^{1}H NMR, and ν_{OH} = 3527 cm^{-1} in the IR). As in other rhenium−oxo complexes,[15,16] proton transfer between the oxo and hydroxide ligands is relatively slow, so three inequivalent pyrazole groups are seen in the ^{1}H and ^{13}C NMR spectra of (HBpz$_3$)ReO(Ph)(OH).



(5)

The phenyl groups in **3**−**5** react with halogens, with the diphenyl complex **5** being particularly reactive. Though **5** is inert to iodine at room temperature, heating it at 80 °C with a large excess of iodine quantitatively forms **4** over the course of several hours (eq 6). Reaction of **4** to form **2** occurs much more slowly under these conditions. In fact, the reaction of **5** with I_2 is the preferred method of synthesis of (HBpz$_3$)ReO(Ph)I.



(6)

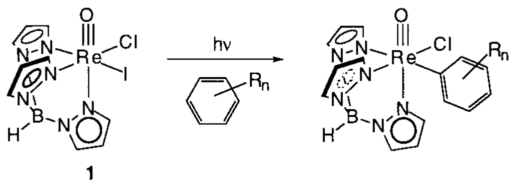
---

(14) Mayer, J. M. *Inorg. Chem.* **1988**, *27*, 3899.

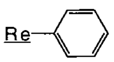
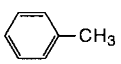
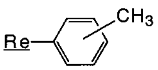
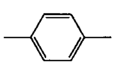
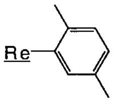
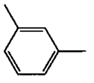
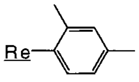
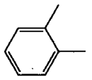
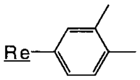
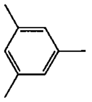
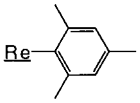
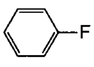
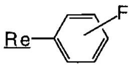
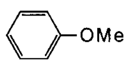
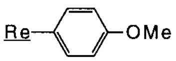
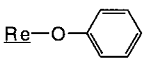
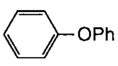
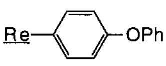
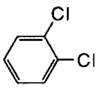
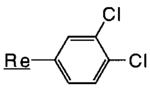
(15) Erikson, T. K. G.; Mayer, J. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1527−1529.

(16) Coe, B. J. *Polyhedron* **1992**, *11*, 1085−1091.

Table 3. Products and Yields for Photochemical Arene Activation by (HBpz$_3$)ReO(Cl)I (1)[a]



1

Entry	Solvent	Products[b]	Yield[a] without py	Yield[a] py added
1			35%	90%
2			37% *m*:*p* = 16:84	79% *m*:*p* = 13:87
3			*c*	72%
4			*c*	28%[d] 95% 2,4-Me$_2$[e]
5			*c*	73% 94% 3,4-Me$_2$[f]
6			*c*	46%
7			32% *o*:*m*:*p* = 43:2:56	88% *o*:*m*:*p* = 41:2:56
8		 	24% 42%	47% 44%
9			*c*	61%
10			*c*	5%[d]

[a] Reactions were performed at approximately 5 mM (HBpz$_3$)ReO(Cl)I in arene solvent (adding about 12 equiv of pyridine where indicated) and irradiated for about 3 days by an Oriel 200 W Hg/Xe lamp with a 455-nm long-pass filter, except for entries 4, 5, 9, and 10, which were irradiated through a thick-walled Pyrex beaker without the 455-nm filter. Yields were determined by integration of ^{1}H NMR spectra against added (Me$_3$Si)$_2$O and are reported relative to the amount of rhenium consumed in the reactions, except where otherwise noted. [b] Re = (HBpz$_3$)Re(O)Cl. [c] Not examined. [d] Isolated yield. [e] 5% of the rhenium product tentatively identified as the 3,5-Me$_2$ isomer. [f] 6% of the rhenium product tentatively identified as the 2,3-Me$_2$ isomer.

Bromine is more reactive than iodine and reacts with **5** at room temperature. However, the major rhenium-containing product of this reaction appears to be the *p*-bromophenyl complex (HBpz$_3$)ReO(*p*-C$_6$H$_4$Br)Br on the basis of its ^{1}H NMR and mass spectra. The organic products produced include benzene, bromobenzene, and brominated biphenyls. Some (HBpz$_3$)ReOBr$_2$[11b] is also formed, but remarkably, cleavage of the C−H bond is competitive with cleavage of the Re−C bond. (HBpz$_3$)ReO(Ph)Cl apparently reacts similarly with bromine (in the presence of pyridine) to give mostly (HBpz$_3$)ReO(*p*-C$_6$H$_4$Br)Cl. This reaction also forms other unidentified aryl complexes which cannot be separated from the main product. While it is unclear whether the halogenations take place via electrophilic cleavage of Re−C or C−H bonds or by radical addition of halogen atoms to the arene, the occurrence of bromoaryl products indicates the inertness of the Re−aryl bond.

Scope and Selectivity of Photochemical Arylation. (HBpz$_3$)ReO(Cl)I (**1**) forms aryl complexes upon photolysis in a variety of aromatic solvents (Table 3). Because of the possibility of forming multiple arylated products, the reactions of **2** were not studied extensively, though (HBpz$_3$)ReO(2,5-Me$_2$C$_6$H$_3$)I was observed on photolyzing the diiodide complex **2** in *p*-xylene. Adding pyridine improves yields without affecting the observed selectivity, as judged by reactions with monosubstituted arenes.

Functionality such as methyl groups or halides may be present on the benzene ring without interfering with arylation. The only case where a functional group is not completely inert is anisole, where there are comparable amounts of C−H activation to form (HBpz$_3$)ReO(*p*-C$_6$H$_4$OMe)Cl and of H$_3$C−O bond cleavage to form the phenoxide complex (HBpz$_3$)ReO(OPh)Cl.[8] In diphenyl ether solvent, **1** is photolyzed only to (HBpz$_3$)ReO(*p*-C$_6$H$_4$OPh)Cl; C−O bond activation is not observed, consistent with the stronger C−O bond in Ph$_2$O. In reactions with methylated benzenes, there is no evidence for benzylic activation, even with the rather hindered mesitylene. In all cases, the methyl substitution pattern of the original arene is retained in the product. The NMR spectra demonstrate increasing barriers to rotation with increasing *ortho*-methyl substitution. Aryl groups without ortho substituents rotate freely, groups with a single *ortho*-methyl group show broadened *o*-CH$_3$ and *o*-H resonances, and the disubstituted mesityl group exhibits sharp, distinct resonances due to inequivalent *ortho*-methyl groups and *meta*-hydrogens.

Arylation takes place with markedly electrophilic selectivity. Toluene gives mostly para substitution, fluorobenzene almost exclusively ortho and para substitution, and anisole and diphenyl ether give only para products. There is some steric preference (e.g., para and not ortho attack is observed with toluene), but it appears at least in certain cases to be outweighed by electronic considerations. Thus, *meta*-xylene (entry 4) reacts to give predominantly the 2,4-isomer, placing the methyl groups ortho and para to the rhenium, with no more than 5% of the sterically more favorable 3,5-isomer. From the admittedly scant database of the meta:para ratios of reactions of toluene and fluorobenzene, it would appear that reactivity of the arenes correlates better with Hammett σ^+ coefficients than with σ coefficients, indicating that substituents may enter into direct resonance stabilization of a positive charge in the product-determining step. The reaction coefficient may be estimated as $\rho^+ \approx -4.3$.

The preference for reactions with electron-rich arenes imposes a significant limitation on the generality of the arylation reaction. Electron-deficient arenes react poorly with **1** under photochemical conditions. α,α,α-Trifluorotoluene, for example, reacts to give only a trace amount of arylrhenium complex (in the absence of pyridine). *ortho*-Dichlorobenzene does form enough product to be isolated, but yields are very low and the reaction requires prolonged photolysis. Evidently, with sufficiently unreactive arenes, alternative reaction pathways can compete for the photogenerated rhenium transient.

Isotope Effects in Photochemical Arylation. To measure isotope effects in the photochemical arylation reaction, **1** was photolyzed in a 1:1 mixture of C$_6$D$_6$ and C$_6$H$_6$ (without added pyridine). The (HBpz$_3$)ReO(Ph)Cl product (**3**) of the reaction was then analyzed by mass spectroscopy to determine the isotopic composition of the phenyl group. Remarkably, the observed ratio of protio to deutero product was found to vary with the concentration of rhenium complex present in solution (Figure 2). At low rhenium concentrations, the ratio of Re−C$_6$H$_5$ to Re−C$_6$D$_5$ product is relatively small, about 1.2:1. As the concentration of rhenium increases, so does the ratio of protio to deutero product, reaching a ratio of about 1.7:1 at [**1**]$_{\text{initial}}$ ≅ 20 mM (a saturated solution in benzene). While the exact values depend on the irradiation conditions, the trend toward higher isotope effects at greater rhenium concentration is unmistakable. Higher isotope effects are generally seen at higher light intensities. The isotope effect also appears to increase with increasing conversion. For example, in one 17.3 mM sample, the Re−C$_6$H$_5$/Re−C$_6$D$_5$ ratio increased smoothly from 1.42 at 3% yield to 1.84 at 20% yield.

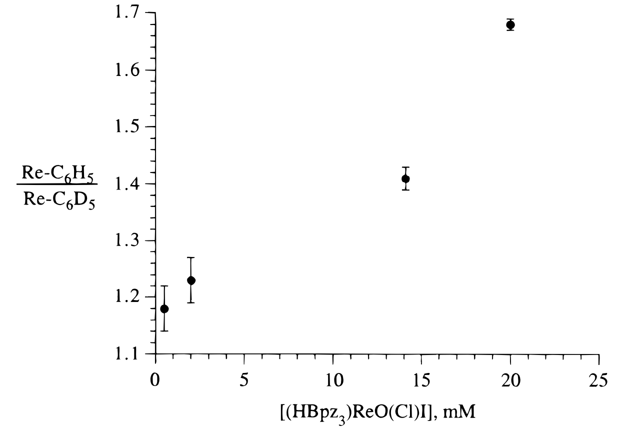


Figure 2. Dependence of observed isotope effect in photochemical arylation on concentration of (HBpz$_3$)ReO(Cl)I (**1**).

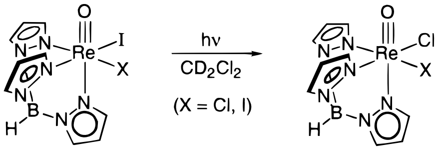
The isotope effect also depends on whether other species are present. In reactions with an initial 19.5 mM concentration of **1**, the addition of 4 equiv of pyridine reduced the isotope effect from 1.8(2) to 1.3. Little effect was observed with solutions 1 mM in rhenium (which have a small isotope effect even in the absence of pyridine). Strangely, the nitrogen bases 2,6-lutidine, trimethylamine, and acetonitrile appear to have a small effect in the opposite direction, increasing the isotope effect (d_0:d_5 = 2.1(1), 2.2(1), and 2.4(2), respectively). The addition of I$_2$ to a 19.5 mM solution of **1** (in the absence of pyridine) increases the isotope effect to 3.5, close to the intramolecular value (see below). In the presence of both I$_2$ and pyridine, the d_0/d_5 ratio was 1.8, similar to that observed in the absence of any additives. Photolysis of 14 mM **1** in the presence of 655 Torr of O$_2$ in 1:1 C$_6$H$_6$/C$_6$D$_6$ gave a 2.1(1):1 ratio of **3**-d_0 to **3**-d_5, slightly higher than observed without O$_2$. Under these conditions, arylation of **1** proceeds with essentially the same yield (32%) as in the absence of O$_2$ but most of the remaining rhenium can be observed under these conditions as (HBpz$_3$)ReO$_3$ (28%) and (HBpz$_3$)ReOCl$_2$ (27%).

The intramolecular isotope effect on this reaction was examined using 1,3,5-trideuteriobenzene as a substrate for photochemical arylation. Irradiation of **1** in neat 1,3,5-C$_6$D$_3$H$_3$ gives both **3**-d_3 (C−H bond broken) and **3**-d_2 (C−D bond broken) in a ratio of 4.0(4):1. In contrast to the intermolecular effect, this larger intramolecular effect is not affected by concentration, from 2.5 to 19.5 mM. Pyridine also has little effect at 19.5 mM **1**, consistent with its lack of an effect on the regiochemistry of attack on substituted benzenes (Table 3) and in contrast to its significant attenuation of the isotope effect discriminating between C_6H_6 and C_6D_6.

The photochemical reaction of $(HBpz_3)ReO(C_6H_5)I$ (**4**) with C_6D_6 has also been examined. In the presence of pyridine, the only isotopomer detectable by FABMS is **5**-d_5, $(HBpz_3)ReO(C_6H_5)(C_6D_5)$. (**5** was analyzed by FABMS because it gives a very weak parent ion in the EI mass spectrum.) In the absence of pyridine, some **5**-d_{10} is observed. However, the d_{10} complex is not observed in reactions that are examined at low conversion but only in those that have gone virtually to completion. Furthermore, in the latter case, the percentage of d_5 product in the trace amount of remaining $(HBpz_3)ReO(Ph)I$ (**4**) is greater than the percentage of d_{10} product in the $(HBpz_3)ReO(Ph)_2$ (**5**) that has formed. This establishes that the mechanism of formation of **5**-d_{10} involves reaction of the initially formed **5**-d_5 with photogenerated HI or I_2 to form **4**-d_5 (*cf.*, eq 6), followed by rearylation to **5**. Thus, there is no loss of the phenyl group in **4** on its conversion to **5**. When **4** was photolyzed in a mixture of C_6H_6 and C_6D_6, a d_0:d_5 ratio of 3.3 was found. This value fell to 2.2 when 4 equiv of pyridine was added.

Discussion

Nature of the Reactive Intermediate. Rhenium(V) oxo iodide complexes **1** and **2** require irradiation with light of 300−500 nm to react with arenes. The primary photoprocess in these reactions appears to be expulsion of iodine atoms. The photoactive bands are intense ($\epsilon \approx 10^3\ M^{-1}\ cm^{-1}$) and are absent in the corresponding chloride complexes. They are, therefore, assigned as iodine-to-rhenium charge-transfer transitions. Metal−iodine bond homolysis is the reaction expected from excitation of iodide-to-metal charge transfer.[17] Consistent with this suggestion, the iodide complexes **1** and **2** are transformed in high yield to rhenium chlorides when photolyzed in dichloromethane (eq 7). Metalloradicals frequently abstract chlorine atoms from chlorinated solvents.[18]



(7)

The metal-containing product following loss of I• from a rhenium(V) iodide complex such as **1** would be a rhenium(IV) complex such as $[(HBpz_3)Re(O)Cl]$. This transient might conceivably undergo subsequent outer-sphere oxidation (e.g., by I•) to form the cationic rhenium(V) complex $[(HBpz_3)Re(O)Cl]^+$. A cationic species is a plausible candidate for undergoing the observed arene activation reactions, since the selectivity is clearly that of an electrophile (Hammett $\rho^+ \approx -4.3$) and since arene activation by cationic metal complexes is precedented.[19] However, several lines of evidence indicate that cationic rhenium(V) species are not involved in arene activation. Most directly, rhenium(V) complexes $(HBpz_3)ReO(X)OTf$ (X = Cl, Ph, or OTf) containing the good leaving group triflate ($CF_3SO_3^-$) have been prepared[9,13] and are all stable indefinitely in benzene solution. No arene activation is ever observed. Adding base to the triflate complexes (to neutralize any HOTf that might be produced) is ineffective at promoting the reaction. In the presence of pyridine (which actually increases the yield in the authentic arene activation reaction), the triflate complexes react in C_6D_6 to precipitate ionic pyridine adducts $[(HBpz_3)ReO(X)py]OTf$ (X = Cl, Ph).[9,13] Addition of triethylamine to $(HBpz_3)ReO(OTf)_2$ in C_6D_6 results in a color change from blue to violet and eventual decomposition on heating the solution, but again no aryl complexes are observed. Finally, the phenyl triflate complex $(HBpz_3)ReO(C_6H_5)OTf$ may be kept in C_6D_6 solution at room temperature for 8 months or heated at 80 °C for 1 month without detectable incorporation of deuterium into the phenyl ligand. This rules out even transitory arene activation, since even fleeting formation of a $Re-C_6D_5$ group would almost certainly lead to exchange with the initial C_6H_5 group.

If cationic species are not involved in arene activation, then the most plausible agent is the direct photoproduct, a rhenium(IV) oxo complex. It should be noted, however, that alternative routes that appear to generate rhenium(IV) oxo species have not led to arene activation. For example, hydrogen-atom abstraction from the rhenium(V) oxo−hydride complex $(HBpz_3)ReO(H)Cl$[20] by triphenylmethyl radical, a procedure that generates metal radicals from other metal hydrides,[21] has been attempted. Triphenylmethane is observed but the rhenium products from this reaction have not been characterized; no arylation to form $(HBpz_3)ReO(Ph)Cl$ is seen in benzene solution. Another reaction that apparently produces the rhenium(IV) transient $[(HBpz_3)Re(O)Cl]$, photolysis of the ethyl complex $(HBpz_3)ReO(C_2H_5)Cl$, also does not produce phenyl products from benzene.[8] Photolyses of benzene solutions of $(HBpz_3)Re(NTol)I_2$, the tolylimido complex analogous to **2**, do not result in significant chemical change such as activation of solvent.[22] In $CDCl_3$ solvent, photolysis slowly gives the chloro−iodide $(HBpz_3)Re(NTol)I(Cl)$, analogous to **2** (eq 7). In summary, the only condition under which these rhenium complexes are observed to react with arenes to form rhenium−carbon bonds is the photolysis of rhenium oxo iodides. This may be due to the unique ability of photochemistry to simultaneously generate both reducing (Re(IV)) and oxidizing (I•) species. Regardless of the details of the mechanism, if a rhenium(IV) species does the actual arene activation, it must be subsequently oxidized to form the observed rhenium-

---

[17] Endicott, J. F. In *Concepts of Inorganic Photochemistry*; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley: New York, 1975; pp 81−142. Stasicka, Z.; Marchaj, A. *Coord. Chem. Rev.* **1977**, *23*, 131−181. See also ref 18, p 329.

[18] Astruc, D. *Electron Transfer and Radical Processes in Transition Metal Chemistry*; VCH: New York, 1995; pp 366−8.

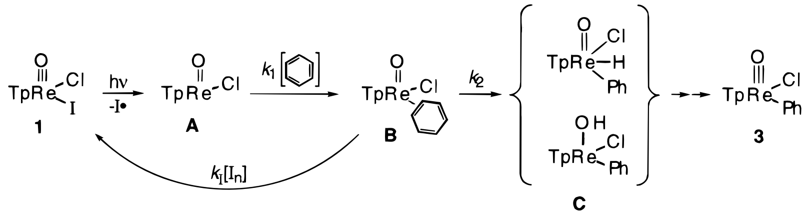
[19] Aoyama, Y.; Yoshida, T.; Sakurai, K.; Ogoshi, H. *Organometallics* **1986**, *5*, 168−173.

[20] Matano, Y.; Brown, S. N.; Northcutt, T.; Mayer, J. M. *Organometallics*, in press.

[21] Eisenberg, D. C.; Lawrie, C. J. C.; Moody, A. E.; Norton, J. R. *J. Am. Chem. Soc.* **1991**, *113*, 4888−4895. See also ref 18, p 330.

[22] Masui, C. S.; Mayer, J. M. *Inorg. Chim. Acta* **1996**, *251*, 325−333.

Scheme 1. Proposed Mechanism for Photochemical Arylation of (HBPz$_3$)ReO(Cl)I^a



^{a} Tp = HBpz$_3$.

(V) products. Such an oxidation would be difficult under the reducing conditions used to generate rhenium(IV) nonphotochemically.

Mechanism of Arene Activation. Three broad conclusions may be drawn from the mechanistic data: (1) *The intermolecular selectivity of the reaction* (as measured by the isotope effect in reactions with C_6H_6/C_6D_6 mixtures) *is highly dependent on the reaction conditions*. The variation of this isotope effect with concentration (Figure 2), as well as with a variety of other additives, is a striking feature of the reaction. The isotope effects range from a low of $k_{C_6H_6}/k_{C_6D_6} \approx 1.2$ at low rhenium concentration or in the presence of pyridine to a high of 3.5 when I_2 is deliberately added to the reaction. Many of the disparate observations can be reconciled by noting that conditions that would be expected to promote elevated I_2 concentrations (addition of I_2 or O_2, high rhenium concentrations, higher conversions) result in elevated isotope effects, while conditions where lower I_2 concentrations might be expected (low rhenium concentrations, low conversions, or pyridine addition, which suppresses decomposition of the rhenium) give lower isotope effects. However, the reasons for a few of the observations (elevated isotope effects in the presence of acetonitrile or lutidine, for example) remain obscure.

Regardless of their origin, the variable isotope effects indicate that arene activation must take place by a multistep mechanism. (The alternative, that several pathways are operating in parallel, is both intrinsically unappealing and inconsistent with point 2 below.) Which step is product determining must be modulated by species in solution such as I_2, $I^\bullet$, and possibly others.

(2) *The intramolecular selectivity of the reaction is independent of the reaction conditions*. In contrast to the variations observed in $k_{C_6H_6}/k_{C_6D_6}$, the intramolecular isotope effect observed for reactions of 1,3,5-$C_6D_3H_3$ remains at 4.0(4), regardless of rhenium concentration or the presence or absence of pyridine. A second measure of intramolecular selectivity, the regioselectivity of attack on toluene or fluorobenzene, is also insensitive to major changes in reaction conditions such as the presence or absence of pyridine. This indicates that discrimination between different sites on a single arene molecule takes place in a single step uniformly under all reaction conditions.

(3) *Cleavage of the C−H bond is effectively irreversible.* This is established conclusively for arene activation by (HBpz$_3$)ReO(Ph)I, since the primary product of C_6D_6 activation by (HBpz$_3$)ReO(C_6H_5)I is exclusively the d_5 isotopomer (HBpz$_3$)ReO(C_6H_5)(C_6D_5). If C−H bond cleavage were significantly reversible under the reaction conditions, one would expect to see fully deuterated product. Since this observation is in essence a statement about relative rates (the intermediate with the C−H bond cleaved must proceed to products much more quickly than it reforms the C−H bond), it is possible that this conclusion does not apply to the reactions of, for example, (HBpz$_3$)ReO(Cl)I. However, given the similarities between the two reactions—notably, the addition of pyridine diminishes the intermolecular isotope effect for the reactions of both species—it is likely that C−H bond cleavage in the latter system is irreversible as well.

A mechanism for arene activation by **1** consistent with these observations is shown in Scheme 1. Absorption of light initiates the chemistry by generating a reactive transient, probably the rhenium(IV) species [(HBpz$_3$)-Re(O)Cl] (**A**). Intermediate **A** then activates arenes in two steps: Coordination without C−H cleavage (k_1) forms **B**, which determines the intermolecular selectivity of the reaction. Then irreversible C−H bond cleavage occurs in **B** (k_2), setting the intramolecular selectivity. The isotope effect on k_2 of 4.0(4) is observed directly in the reaction of neat 1,3,5-$C_6H_3D_3$ (there can be no intermolecular partitioning in this case) and is consistent with a primary isotope effect, as expected for breaking a C−H bond. The isotope effect on k_1 corresponds to the lower limit observed for the intermolecular isotope, so $k_{1H}/k_{1D} \leq 1.2$, consistent with a secondary isotope effect. This mechanism parallels the observations of Jones and co-workers on oxidative addition of arenes to rhodium(I) species. For example, [Cp*Rh-(PMe$_3$)] reacts with arenes by rate-limiting arene coordination, with a $k_{C_6H_6}/k_{C_6D_6}$ of 1.05, followed by oxidative addition of an arene C−H bond with $k_H/k_D = 1.4$.[5c,d] Furthermore, the ability of the metal to access all sites on the arene in the coordinated intermediate, required here to explain the invariant *o*:*m*:*p* ratio of attack on fluorobenzene, has been documented in the reactions of (HB[3,5-Me$_2$pz]$_3$)Rh(CNCH$_2{}^t$Bu)(Ph)(H).[23]

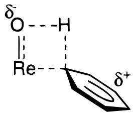
A simple scenario of reversible binding followed by irreversible cleavage is not adequate to explain the observed variation in intermolecular isotope effect. In order for external agents to shift the balance between the first and second steps, they must affect the ratio of k_2/k_{-1}. This might occur if they were directly involved in breaking the C−H bond; $I^\bullet$ might abstract a hydrogen atom from the coordinated arene, for instance. However, this would mean that at high concentrations of $I^\bullet$, the second step would become relatively fast and arene coordination would become more product determining, which would tend to *decrease* the observed isotope effect. The opposite is observed, which suggests that external agents are affecting k_{-1} rather than k_2. In a formal

---

(23) Jones, W. D.; Hessell, E. T. *J. Am. Chem. Soc.* **1992**, *114*, 6087−6095.

sense, this represents catalysis of arene exchange in **B**. A more chemically sensible explanation might be that I_2 or $I^\bullet$ could oxidize the arene adduct to a cationic species, with subsequent displacement of arene by iodide ion, regenerating starting material. This is indicated in Scheme 1 by the curved arrow labeled k_I-$[I_n]$. Surprisingly, uncatalyzed arene exchange of **B** must not be able to compete with C−H activation. If it could, then arene exchange would occur under all conditions and the k_1 step could never be product determining.

The C−H activation step (k_2) could be oxidative addition to rhenium or $[2_\sigma + 2_\pi]$ addition to the Re═O bond. We favor the latter (drawn below) because of its electrophilic regiochemistry,



as revealed in the preference for para over meta activation of toluene and fluorobenzene ($\rho^+ \approx -4.3$). Oxidative addition of C−H bonds do not typically show significant polar effects.[24] In contrast, the $[2_\sigma + 2_\pi]$ addition of a C−H bond process is thought to be very polar, involving electrophilic attack of the metal at carbon with proton removal by an internal base, here the oxo ligand. Activation of C−H bonds by early-transition-metal d^0 terminal imido complexes has only been observed when the metal center is very electrophilic,[7] and the importance of this has been highlighted theoretically.[25] The basicity of the terminally bound ligand also appears to be important in these early-transition-metal systems. For example, $[Cp_2Zr(N^tBu)]$ will activate benzene[7d,e] while the closely related $[Cp^*_2Zr(O)]$, with a less basic oxo ligand, will not.[26] High basicity of the oxo group is reasonable for a d^3 oxo complex such as **B**.[27] This polar description is to be contrasted with the addition of a rhenium "radical" to the arene, for this kind of reaction would be expected to share the generally low selectivity displayed by organic radicals' addition to aromatic compounds.[28]

Conclusions

Photolysis of the rhenium(V) oxo−iodide complexes $(HBpz_3)ReO(I)Cl$ (**1**) and $(HBpz_3)ReOI_2$ (**2**) in arene solvents results in replacement of the iodide ligand by an aryl group. This is the first example of formation of an isolable oxo−alkyl or −aryl complex from a metal oxo complex and a hydrocarbon. Arene activation occurs exclusively at aromatic rather than benzylic positions, has some functional group tolerance, and shows marked electrophilic selectivity. The addition of pyridine improves the yield of aryl products but does not affect the regiochemistry of arylation. The intermolecular isotope effect observed on irradiation of **1** in mixtures of C_6H_6 and C_6D_6 ranges from $k_{C_6H_6}/k_{C_6D_6} = 1.2$ to 3.5, depending on the concentration of rhenium and on the presence of other reagents such as pyridine or I_2. The isotope effect from intramolecular competition in 1,3,5-$C_6H_3D_3$ is larger (4.0(4)) and insensitive to the details of the reaction conditions. These and related data indicate a mechanism with two product-determining steps, such as Scheme 1. Changing the photolysis conditions changes the amount that each step is product determining, thus changing the (intermolecular) isotope effect. At low rhenium concentrations (or in the presence of pyridine), the product is determined by a step with a very low intermolecular isotope effect, ≤1.2, which is suggested to be arene coordination. The subsequent C−H activation step is more product determining at higher rhenium concentrations and in the presence of added I_2 and is the source of the intramolecular isotope effect. The changing reaction conditions affect the rate of arene decoordination; in the absence of additives (particularly I_2), C−H activation is significantly faster than dissociation of the arene. C−H activation is proposed to take place by addition of the C−H bond across the Re═O bond, with subsequent oxidation of the Re−OH to give the final oxo−aryl product.

Experimental Section

Unless otherwise noted, reactions were set up using standard vacuum line or inert atmosphere glovebox techniques. Purification was done on the benchtop using commercial samples of solvents since all compounds prepared are air- and water-stable. Aromatic solvents were dried over sodium, except fluorobenzene, which was dried over P_2O_5, and 1,2-dichlorobenzene, which was distilled from CaH_2. Pyridine was dried over CaH_2, MeCN and CH_2Cl_2 over 4 Å molecular sieves followed by CaH_2, and tetrahydrofuran (THF) from sodium benzophenone ketyl. All solvents were vacuum transferred from their drying agents before use and were stored in the drybox if not used immediately. $(HBpz_3)ReOCl_2$,[11] the oxo−phenyl complexes $(HBpz_3)ReO(Ph)I$ (**4**) and $(HBpz_3)ReO(Ph)_2$ (**5**),[9] and $(Ph_3C)_2$ (Gomberg's dimer)[29] were prepared by literature procedures. Other reagents were commercially available and used without further purification.

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian VXR-300 or Bruker AF-300 spectrometer at 300 or 75.4 MHz, respectively. ^1H NMR spectra are given in Table 4. ^{19}F NMR spectra were recorded on a Varian VXR-300 (282.203 MHz) or Bruker AC-200 (188.298 MHz) spectrometer and referenced to external CF_3COOH at 0 ppm. IR spectra were obtained on a Perkin-Elmer 1604 FT-IR spectrometer; peaks are reported in wavenumbers. The $HBpz_3$ ligand gives rise to a large number of bands that do not vary significantly from compound to compound: 3112 (m), 1503 (m), 1409 (s), 1312 (s), 1212 (s), 1116 (s), 1072 (m), 1051 (vs), 987 (w), 762 (s), 715 (s), 657 (m), 615 (m). Fast-atom bombardment and electron-impact mass spectra (FABMS and EIMS) were acquired as previously described.[9] Elemental analyses were performed by Canadian Microanalytical Services, Ltd., Vancouver, BC.

$(HBpz_3)ReO(Cl)I$ (1). Method A. A mixture of $(HBpz_3)ReOCl_2$ (345 mg, 0.71 mmol) and NaI (120 mg, 0.80 mmol, 1.13

---

(24) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. For instance, toluene C−H oxidative addition to $Cp^*Rh(PMe_3)$ gives the statistical 2:1 ratio of *meta*:*para* isomers: Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650. Greater selectivity (m:p = 1:1.75) is observed with $[Os(PMe_3)_2\{P(OMe)_3\}_2]$: Werner, H.; Gotzig, J. *J. Organomet. Chem.* **1985**, *284*, 73−93. Observed here is m:p = 1:6.

(25) Cundari, T. R. *J. Am. Chem. Soc.* **1992**, *114*, 10557−10563.

(26) (a) Carney, M. J.; Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 8751−8753. Carney, M. J.; Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1992**, *11*, 761−777. (b) Howard, W. A.; Waters, M.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 4917−4918.

(27) Mayer, J. M. *Comm. Inorg. Chem.* **1988**, *8*, 125.

(28) Perkins, J. M. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, pp 231−271.

(29) Volz, H.; Lotsch, W.; Schnell, H.-W. *Tetrahedron* **1970**, *26*, 5343−5352.

Table 4. ^{1}H NMR Data for (HBpz$_3$)Re(O)XY Compounds[a]

compound	pz triplets	pz doublets	aryl resonances
TpReO(Cl)I (**1**)	5.95, 6.57, 6.59	7.40, 7.49, 7.93, 7.96, 8.19, 8.58	
TpReOI$_2$ (**2**)	5.90, 6.56 (2H)	7.41, 7.54, 7.94 (2H), 8.61 (2H)	
TpReO(Ph)Cl (**3**)[b]	5.16, 5.64, 5.76	6.69, 6.95, 7.07, 7.12, 7.23, 8.39	7.02 (t, 8 Hz, 1H; *p*), 7.45 (t, 8 Hz, 2H; *m*), 7.76 (d, 8 Hz, 2H; *o*)
TpReO(Ph)I (**4**)[h]	5.88, 6.44, 6.54	7.13, 7.41, 7.46, 7.91, 7.95, 8.77	6.85 (t, 7 Hz, 1H; *p*), 7.15 (d, 8 Hz, 2H; *o*), 7.35 (t, 8 Hz, 2H; *m*)
TpReO(Ph)$_2$ (**5**)[b,h]	5.92, 6.42 (2H)	6.75,[c] 7.52, 7.70 (2H), 7.94 (2H)	6.75[c] (m, 2H; *p*), 6.99 (d, 7 Hz, 4H; *o*), 7.31 (t, 8 Hz, 4H; *m*)
TpReO(Ph)(OH)[d,e]	5.82, 6.39, 6.48	6.83, 7.33, 7.71, 7.83, 7.90, 8.24	7.13 (tt, 7 and 1 Hz, 1H; *p*), 7.28 (dd, 8 and 1 Hz, 2H; *o*), 7.42 (t, 7 Hz, 2H; *m*)
TpReO(*p*-C_6H_4Br)Br[d]	5.84, 6.44, 6.51	6.76, 7.36, 7.49, 7.84, 7.87, 8.56	7.10, 7.46 (each d, 8 Hz, 2H)
TpReO(*p*-C_6H_4Br)Cl[f]	5.91, 6.54, 6.61	6.76, 8.07, 8.07, 8.39[g]	7.11, 7.51 (each d, 6 Hz, 2H)
TpReO(2,5-$Me_2C_6H_3$)Cl[d]	5.89, 6.39, 6.51	7.13, 7.40, 7.44, 7.84, 7.91, 8.35	6.01 (br s, 1H; 6-*H*), 6.60 (d, 7 Hz, 1H; 4-*H*), 7.52 (d, 8 Hz, 1H; 3-*H*), 3.11 (br s, 3H; 2-*Me*), 1.88 (s, 3H; 5-*Me*)
TpReO(2,5-$Me_2C_6H_3$)I[b]	5.25, 5.56, 5.81	6.72, 7.08, 7.40, 8.67[g]	5.98 (br s, 1H; 6-*H*), 6.58 (d, 8 Hz, 1H; 3-*H*), 7.81 (d, 8 Hz, 1H; 4-*H*), 3.72 (br s, 3H; 2-*Me*), 1.88 (br s, 3H; 5-*Me*)
TpReO(2,4,6-$Me_3C_6H_2$)Cl[b]	5.19, 5.64, 5.78	6.73, 7.06, 7.13, 7.21, 7.24, 8.16	7.11, 7.62 (s, 1H; Ar*H*), 3.88, 2.69, 1.30 (s, 3H; ArC*H*$_3$).
TpReO(*p*-$C_6H_4CH_3$)Cl[f]	5.88, 6.53, 6.59	6.73, 7.49, 7.54, 8.05, 8.08, 8.38	7.12, 7.20 (d, 8 Hz, 2H; Ar*H*), 2.55 (s, 3H; ArC*H*$_3$)
TpReO(*m*-$C_6H_4CH_3$)Cl[f]	5.89, 6.53, 6.59	6.77, 7.48, 7.54, 8.05, 8.08, 8.38	6.83, 6.85 (each br d, 8 Hz, 1H, 4-*H*, 6-*H*), 7.17 (br s, 1H; 2-*H*), 7.24 (t, 8 Hz, 1H; 5-*H*), 2.15 (s, 3H; ArC*H*$_3$)
TpReO(*o*-C_6H_4F)Cl	5.91, 6.47, 6.57	7.01, 7.46, 7.54, 7.94, 7.95, 8.39	6.76 (ddd, 7 Hz, 6, 2, 1H; 6-*H*), 7.25 (td, 8 Hz, 1, 1H; 3-*H* or 5-*H*)[g]
TpReO(*p*-C_6H_4F)Cl	5.86, 6.50, 6.56	6.82, 7.44, 7.56, 8.42, 7.94 (2H)	7.08 (t, 9, 2H; 3,5-*H*), 7.33 (dd, 9, 6, 2H; 2,6-*H*)
TpReO(*p*-$C_6H_4OCH_3$)Cl[d]	5.82, 6.46, 6.51	6.88, 7.35, 7.61, 8.44, 7.86 (br 2H)	6.94, 7.36 (d, 9, 2H; Ar*H*), 3.85 (s, 3H; OC*H*$_3$)
TpReO(2,4-$Me_2C_6H_3$)Cl	5.92, 6.42, 6.55	7.07, 7.40, 7.46, 7.91, 7.96, 8.33	6.13 (br d, ~6, 1H; 6-*H*), 6.84 (d, 7 Hz, 1H; 5-*H*), 7.48 (s, 1H; 3-*H*), 3.11 (br s, 3H; 2-*Me*), 2.70 (s, 3H; 4-*Me*)
TpReO(3,4-$Me_2C_6H_3$)Cl[d]	5.77, 6.39, 6.45	6.91, 7.33, 7.56, 7.82, 7.83, 8.41	6.85 (dd, 8 and 1 Hz, 1H; 6-*H*), 7.13 (d, 8 Hz, 1H; 5-*H*), 7.38 (s, 1H; 2-*H*), 2.15 (s, 3H; 3-*Me*), 2.50 (s, 3H; 4-*Me*)
TpReO(3,4-$Cl_2C_6H_3$)Cl[d]	5.85, 6.48, 6.52	6.87, 7.37, 7.57, 7.87, 7.89, 8.42	7.07 (dd, 8 and 2 Hz, 1H; 6-*H*), 7.40 (d, 8 Hz, 1H; 5-*H*), 7.41 (br s, 2-*H*)
TpReO(*p*-C_6H_4OPh)Cl[d]	5.82, 6.45, 6.50	6.91, 7.35, 7.62, 8.43, 7.85 (2H)	7.01, 7.34 (d, 9 Hz, 2H; Re−C$_6$*H*$_4$OPh), 7.06 (d, 8 Hz, 2H; *o*-OPh), 7.08 (t, 8 Hz, 1H; *p*-OPh), 7.32 (t, 7 Hz, 2H; *m*-OPh)

[a] Tp = HBpz$_3$; spectra in CD$_2$Cl$_2$ unless otherwise specified; chemical shifts in δ. Each pyrazole resonances has a 2 Hz coupling constant and integrates to 1 hydrogen, unless otherwise specified. Aryl resonances are given as chemical shift (multiplicity, coupling constant, number of hydrogens; assignment). [b] Spectrum in C$_6$D$_6$. [c] pz doublet and aryl resonance overlap. [d] Spectrum in CDCl$_3$. [e] −Re−O*H*: 13.56 (s, 1H). [f] Spectrum in CD$_3$CN. [g] Two resonances are obscured. [h] From reference 9.

equiv) were dissolved in 50 mL of CH$_3$CN in the air and refluxed for 3 days. The solvent was stripped off, and the green residue was dissolved in CH$_2$Cl$_2$ (50 mL). After washing twice with a similar volume of water, the CH$_2$Cl$_2$ layer was dried over MgSO$_4$ and stripped dry. The residue was dissolved in a minimum volume of CH$_2$Cl$_2$ and loaded onto a large (8 cm × 8 cm diameter) column of silica gel. Careful chromatography, eluting with toluene, allowed the separation of the fastest moving yellow band of **2** (see below) from the slower moving green band of the desired **1** and from a yet slower moving blue band due to unreacted (HBpz$_3$)ReOCl$_2$. The green band was collected and the toluene removed to give 102 mg of **1** (25%). The analytical sample was crystallized from toluene/hexane. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 106.5, 109.0, 109.4, 135.1, 139.3, 139.6, 146.6, 149.9, 151.0. IR: 2518 (m; ν_{BH}), 977 (s; ν_{ReO}) cm^{-1}. UV−vis (CH$_3$CN): λ_{max} = 698 nm (ϵ = 120 M^{-1} cm^{-1}), 420 sh (910), 366 (2400), 292 sh (5800), 264 (8900), 250 sh (8800). FABMS: 578 (M + H). Anal. Calcd for C$_9$H$_{10}$BClIN$_6$ORe: C, 18.71; H, 1.74; N, 14.55. Found: C, 18.76; H, 1.76; N, 14.61.

Method B. Better yields can be obtained by a slightly less convenient route. In the drybox, (HBpz$_3$)ReOCl$_2$ (719 mg, 1.48 mmol), AgOTf (Aldrich; 384 mg, 1.49 mmol, 1.01 equiv), and a stirbar were placed in a glass bomb with a Teflon needle valve. The flask was taken to the vacuum line, and ~40 mL of CH$_2$Cl$_2$ was vacuum transferred onto the solids. The sealed container was heated at 80 °C for 2.5 h. The bomb was returned to the drybox, and the solution was filtered through a plug of glass wool into a solution of 625 mg of NaI (4.17 mmol, 2.8 equiv) in 50 mL of dry CH$_3$CN. This brown solution was stirred for 5 h, then opened to the air, and the solvent was stripped off. The brown powder was extracted with CH$_2$Cl$_2$ and filtered through a plug of silica gel to remove sodium salts and a brown impurity. The deep green filtrate was concentrated and purified by careful chromatography, as described above, to give 413 mg (48%) of **1**.

(HBpz$_3$)ReOI$_2$ (2). Into a 250-mL round-bottom flask in the air were placed a magnetic stirbar, (HBpz$_3$)ReOCl$_2$ (1.14 g, 2.34 mmol), NaI (4.41 g, 29.4 mmol), and 120 mL of MeCN. The mixture was refluxed for 2 days, and the solvent was removed. The yellow-brown residue was taken up in 70 mL of CH$_2$Cl$_2$ and gravity-filtered to remove sodium salts. The volume of the filtrate was reduced to 30 mL, and it was filtered through a pad of silica gel, washing the silica with more CH$_2$Cl$_2$ to remove a reddish impurity. This solution is about 90% pure **2**. To drive the reaction to completion, the solution was stripped down, taken up in 150 mL of CH$_3$CN, and refluxed with 4.37 g of NaI for 5 more days. After stripping down, taking up in CH$_2$Cl$_2$, gravity-filtering, and filtering through silica as described above, the dark yellow material was recrystallized from a minimum volume of hot CH$_3$CN. The dense black microcrystals that were deposited overnight at room temperature were washed with a small portion of CH$_3$CN and then with 2 × 15 mL hexane to give 0.765 g of **2** (49%). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 106.5, 135.0, 152.4 (pyrazole trans to oxo), 109.3, 139.2, 150.1 (pyrazoles trans to iodine). IR: 2517 (m; ν_{BH}), 977 (s; ν_{ReO}) cm^{-1}. UV−vis (CH$_3$CN): λ_{max} = 708 nm (ϵ = 140 M^{-1} cm^{-1}), 490 sh (370), 410 sh (2100), 348 sh (3900), 304 sh (5400), 260 (8200). FABMS: 671 (M + H). Anal. Calcd for C$_9$H$_{10}$BI$_2$N$_6$ORe: C, 16.16; H, 1.51; N, 12.56. Found: C, 16.23; H, 1.42; N, 12.58.

(HBpz$_3$)ReO(Ph)Cl (3). (HBpz$_3$)ReO(Cl)I (118 mg, 0.20 mmol) was weighed into a 50-mL round-bottom flask with a stirbar and capped with a Teflon needle valve. Into this was vacuum-transferred 35 mL of dry benzene, and in the drybox 200 μL of dry pyridine was added. The solution was degassed and then photolyzed (Oriel 200 W Hg/Xe lamp) for 1 week while stirring in a Pyrex beaker filled with water (to moderate the temperature). The brown solution was filtered in the drybox to remove pyH^+I^-, and the solution was taken out into the air. The brown solution was chromatographed in portions through Pasteur pipets filled with silica gel, eluting with toluene, collecting the dark blue material in several fractions (prolonged exposure to silica drastically reduces the yield). The purity of the fractions was checked by TLC, and they were rechromatographed as necessary. Stripping down the eluate gave 67 mg (62%) of **3**. The analytical sample was crystallized from toluene/hexane. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 105.7, 108.2, 108.9, 134.7, 138.4, 139.7, 146.4, 147.0, 148.9 (pz), 154.9 (*ipso*), 144.8 (*ortho*), 129.8 (*para*), 126.4 (*meta*). IR: 2520 (m, ν_{BH}), 978 (s, ν_{ReO}), 845 (m), 782 (m), 738 (m), 695 (m), 667 (m) cm^{-1}. UV−vis (CH_3CN): $\lambda_{max} = 661$ nm ($\epsilon = 120$ M^{-1} cm^{-1}), 321 sh (3000), 248 (1.2×10^4). EIMS: 528 (M^+). Anal. Calcd for $C_{15}H_{15}BClN_6ORe$: C, 34.14; H, 2.86; N, 15.92. Found: C, 34.40; H, 2.90; N, 15.99.

(HBpz$_3$)ReO(Ph)(OH). To a slurry of 2.55 g of silica gel slurried in 6 mL of toluene was added 60 mg of **3** in 5 mL of toluene. After 1 h, additional silica gel slurried in toluene was added in small portions until the supernatant was practically colorless. The slurry was then poured onto a glass frit and washed with toluene until the eluate was colorless. Crude product was washed off the silica gel with EtOAc and promptly chromatographed on a Pasteur pipet filled with silica gel. CH_2Cl_2/EtOAc (25:1 v/v) eluted, first, a yellow compound and then the desired complex as a violet band. The solution was promptly stripped down, taken up in 1 mL of toluene, which was layered with 8 mL of hexane, and allowed to stand at −20 °C for 2 days to give 18.1 mg (31%) of violet crystals. The compound is stable in the solid state but decays over a day or so in solution in the presence or absence of air to form uncharacterized materials. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 105.3, 107.8 (2 C), 133.7, 137.8, 138.0, 144.3, 144.8, 148.7 (pzs), 153.9, 141.7, 129.0, 127.4 (Ph, *i*, *o*, *p*, *m*). IR (Nujol mull): 3527 (sharp, m, ν_{OH}), 3360 (br, m, ν_{OH}), 2518 (m, ν_{BH}), 1127 (m), 977 (s, ν_{ReO}), 950 (s), 784 (w), 764 (s) cm^{-1}. EIMS: 510 (M^+).

(HBpz$_3$)ReO(*p*-C$_6$H$_4$Br)Br was obtained on treatment of **5** (4.4 mg, 7.7 μmol) in 0.5 mL of $CDCl_3$ with ∼2 μL of Br_2 for 25 h, followed by flash chromatography on silica (C_6H_6). $(HBpz_3)Re(O)Br_2$, $(HBpz_3)Re(O)Br(Cl)$, and brominated organic products are also formed. EIMS: 652 (M^+). **(HBpz$_3$)ReO(*p*-C$_6$H$_4$Br)Cl** was prepared in a similar manner from **3** (7.0 mg, 13.3 μmol), 0.3 μL of pyridine, 0.4 mL of $CDCl_3$, and 1.5 μL of Br_2 (∼29 μmol). After 24 h, another 3 μL of py and 2 μL of Br_2 was added and the product isolated by flash chromatography on silica (C_7H_8).

General Procedure for Small-Scale Photochemical Arylations. In a typical procedure, about 25 mg of $(HBpz_3)ReO(Cl)I$, 40 μL of pyridine, 8 mL of the appropriate arene solvent, and a stirbar were placed in a 10 mL round-bottom flask in the drybox. The flask was sealed with a Teflon needle valve and degassed on the vacuum line. The flask was then placed in a Pyrex beaker filled with water and photolyzed with stirring using a 200-W Hg/Xe arc lamp (Oriel), often with the light filtered through a 455-nm long-pass filter (Oriel). After 3−4 days of photolysis, the volatiles were removed from the flask and the residue analyzed by ^1H NMR. If desired, the residue was purified by chromatography on a short column of silica gel.

(HBpz$_3$)ReO(2,5-Me$_2$C$_6$H$_3$)Cl was obtained from photolysis of **1** in *p*-xylene. $^{13}C\{^1H\}$ NMR: δ 105.7, 107.9, 108.7, 134.2, 137.3, 139.3, 145.8, 147.5, 149.7 (pyrazoles), 145.3, 131.2, 130.5, 127.2 (aryl), 21.3 ($-CH_3$). (Not all resonances are observed, presumably due to broadening due to partially restricted rotation about the Re−C bond.) IR (evaporated film): 2516 (m, ν_{BH}), 981 (s, ν_{ReO}), 954 (m), 910 (m), 810 (m), 791 (m), 668 (m) cm^{-1}. EIMS: 556 (M^+). **(HBpz$_3$)ReO(2,6-Me$_2$C$_6$H$_2$)I** was obtained in very low yield on photolysis of **2** in *p*-xylene for 65 h followed by multiple flash chromatography on silica (C_6H_6). EIMS: 648 (M^+). **(HBpz$_3$)ReO(2,4,6-Me$_3$C$_6$H$_2$)Cl** was obtained from photolysis of **1** in mesitylene. IR (evapd film): 2502 (m, ν_{BH}), 1596 (w, $\nu_{C=C}$), 979 (s, ν_{ReO}). EIMS: 570 (M^+). **(HBpz$_3$)ReO(C$_6$H$_4$-CH$_3$)Cl** was obtained from photolysis of **1** in toluene as a mixture of isomers. EIMS: 542 (M^+). **(HBpz$_3$)ReO(C$_6$H$_4$F)Cl** was obtained from photolysis of **1** in fluorobenzene as a mixture of isomers, with the meta isomer in insufficient quantity to assign its ^1H NMR spectrum. EIMS: 546 (M^+). ^{19}F NMR (C_6D_6): ortho isomer δ −2.98 (dt, 8, 5 Hz); meta isomer δ −36.12 (td, 9, 6 Hz); para isomer δ −34.24 (tt, 9, 6 Hz).

(HBpz$_3$)ReO(*p*-C$_6$H$_4$OCH$_3$)Cl was prepared by photolysis of 50.6 mg of **1** and 90 μL of pyridine in 5 mL of anisole. The aryl complex is formed along with a comparable amount of the phenoxide complex $(HBpz_3)ReO(OPh)Cl$.[8] The two complexes have very similar R_f values in toluene and can only be separated laboriously after repeated chromatography on silica gel. $(HBpz_3)ReOCl_2$ is a minor byproduct, which could not be separated from the aryl complex and persisted as a ca. 5% impurity in the 11.6 mg of $(HBpz_3)ReO(p\text{-}C_6H_4OMe)Cl$ (24%; 74% recovery based on NMR yield of product) isolated by crystallization of the chromatographed material from hot heptane. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 105.5, 107.8, 108.5, 133.9, 137.6, 138.9, 146.3, 146.9, 148.5 (pyrazoles), 161.4 (*ipso*), 146.6 (*ortho*), 146.5 (*para*), 111.7 (*meta*), 55.0 (OCH_3). IR (evapd film): 2517 (m, ν_{BH}), 1578 (m, $\nu_{C=C}$), 1488 (m), 1271, 1241 (m, ν_{C-O}), 980 (s, ν_{ReO}), 817 (w), 790 (w), 736 (w), 668 (w) cm^{-1}. UV−vis (CH_3CN): $\lambda_{max} = 660$ nm ($\epsilon = 200$ M^{-1} cm^{-1}), 356 (4900), 246 (1.4×10^4). EIMS: 558 (M^+).

(HBpz$_3$)ReO(2,4-Me$_2$C$_6$H$_3$)Cl was synthesized by photolyzing 172 mg of **1** and 300 μL of pyridine in 35 mL of *m*-xylene for 8 days. The reaction mixture was chromatographed in the usual way, and the TLC-pure fractions were crystallized from toluene/hexane to yield 46.8 mg of $(HBpz_3)ReO(2,4\text{-}Me_2C_6H_3)$ (28%). The material contains a small amount (<5%) of the 3,5-isomer as well. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 105.9, 108.2, 109.1; 134.8, 138.0, 139.93, 146.0, 147.8, 149.9 (pzs), 157.6 (br, *ipso*), 147.4 (br, 2-C), 145.3 (6-C), 139.91 (4-C), 128.4, 123.7 (3-, 5-C), 27.4 (br, 2-CH_3), 20.3 (4-CH_3). IR (Nujol mull): 2485 (m, ν_{BH}), 1594 (w), 980 (s, ν_{ReO}), 921 (w), 889 (w), 867 (w), 808 (m), 783 (w), 674 (w) cm^{-1}. EIMS: 556 (M^+), 520 ($M^+ - Cl$), 435 ($[HBpz_3]ReCl^+$).

(HBpz$_3$)ReO(3,4-Me$_2$C$_6$H$_3$)Cl was prepared from *o*-xylene in a manner analogous to that described for the reaction of *m*-xylene described above. $(HBpz_3)ReO(Cl)I$ (177 mg, 0.306 mmol) and pyridine (300 μL) were dissolved in 25 mL of *o*-xylene and photolyzed for 3 days. The solution was then filtered through a glass frit in the drybox, and the filtrate was photolyzed 5 more days. After chromatography, crystallization from toluene yielded 70.6 mg of blue-green $(HBpz_3)ReO(3,4\text{-}Me_2C_6H_3)Cl\cdot C_7H_8$ (36%). Although a small amount (6%) of a minor component, probably the 2,3-isomer, is present in the reaction mixture, this component does not crystallize with the major isomer. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 105.4, 107.8, 108.4, 133.9, 137.5, 138.9, 145.5, 146.8, 148.5 (pzs), 152.5 (*ipso*), 146.1, 142.6 (C-2 and C-6), 138.2, 133.5 (C-3 and C-4), 127.3 (C-5), 19.2, 20.1 (3- and 4-CH_3). IR (evapd film): 2919 (w, ν_{CH}), 2513 (m, ν_{BH}), 1390 (m), 1265 (w), 980 (s, ν_{ReO}), 891 (w), 815 (w), 791 (w), 736 (w) cm^{-1}. EIMS: 556 (M^+), 449, 435 ($[HBpz_3]ReCl^+$).

(HBpz$_3$)ReO(3,4-Cl$_2$C$_6$H$_3$)Cl. In the drybox, **1** (167.6 mg, 0.290 mmol) and 300 μL of pyridine were dissolved in 30 mL of *o*-dichlorobenzene. The solution was degassed on the vacuum line and photolyzed in the usual fashion for 14 days. The reaction proceeds very slowly with this electron-deficient arene, and substantial amounts of $(HBpz_3)ReOCl_2$ and $(HBpz_3)ReOI_2$ are also produced in a competitive photochemical disproportionation reaction. After removing the solvent on the vacuum line, the aryl complex was separated from the contaminating halide complexes by chromatography in 2:1 toluene:hexane, in which solvent the desired complex is the most rapidly moving band. Repeated chromatography nets only 8 mg (5%) of deep blue (HBpz$_3$)ReO(3,4-Cl$_2$C$_6$H$_3$)Cl; none of the other regioisomer is observed. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 105.9, 108.1, 108.9, 134.4, 138.0, 139.3, 145.5, 146.7, 148.3 (pzs), 152.3 (C-1), 146.3, 143.6 (C-2, C-6), 133.3, 130.3 (C-3, C-4), 127.8 (C-5). IR (evapd film): 2520 (m, ν_{BH}), 1456 (m), 1390 (m), 1024 (m), 982 (s, ν_{ReO}), 814 (w), 668 (m) cm^{-1}. EIMS: 596 (M$^+$), 449, 435 ([HBpz$_3$]ReCl$^+$).

(HBpz$_3$)ReO(*p*-C$_6$H$_4$OPh)Cl. **1** (115.3 mg, 0.200 mmol) and 190 μL of pyridine were photolyzed as usual in diphenyl ether for 3 days, then 3 more days after filtration in the drybox to remove pyridinium iodide. The solvent was removed by distillation at reduced pressure (the bath temperature reaches 80°). The residue is chromatographed repeatedly in Pasteur pipets filled with silica gel, eluting with 2:1 toluene:hexane, to separate the blue-green aryl complex from a faster moving yellow impurity and a slower moving green band. Yield of chromatographically pure material: 50 mg (40%). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 105.6, 107.9, 108.6, 134.0, 137.7, 139.0, 146.2, 146.9, 148.5 (pzs), 157.4, 159.2 (C-1 and C-1′), 146.5 (C-2,6), 116.3 (C-3,5), 148.6 (C-4), 119.2 (C-2′,6′), 129.6 (C-3′,5′), 123.1 (C-4′). IR (evapd film): 2515 (m, ν_{BH}), 1570 (s, $\nu_{C=C}$), 1238 (s, ν_{C-O}), 981 (s, ν_{ReO}), 867 (w), 694 (w) cm^{-1}. EIMS: 620 (M$^+$).

Isotope Effect Measurements. In a typical experiment, 21.7 mg of **1** was dissolved in 1.93 mL of a 1:1 (v/v) mixture of C$_6$H$_6$ and C$_6$D$_6$ in the glovebox. The Pyrex flask was capped with a Teflon needle valve apparatus and photolyzed (Oriel 200 W Hg/Xe lamp) for 3 days. The volatiles were then removed in vacuo. The residue was analyzed by mass spectroscopy (direct inlet, electron ionization), analyzing the full isotope patterns and/or the parent ions of d_0- vs d_5-**3**. In some cases, the residue was analyzed by NMR, for instance experiments using C$_6$H$_3$D$_3$, because of the overlapping isotope patterns of d_2- vs d_3-**3**. The reported errors are 1σ values from repeated photolyses and/or repeated mass spectral analyses of the same residue. The isotope effects in Figure 2 were confirmed by three different researchers over a >2 year period.

X-ray Crystallography of (HBpz$_3$)ReO(Ph)$_2$ (5). Small blue blocks of **5** were grown by allowing a solution in hot hexane/Me$_3$SiOSiMe$_3$ to cool slowly to room temperature. A crystal was stuck with epoxy to the tip of a glass fiber and examined on an Enraf-Nonius CAD4 diffractometer; crystallographic data are summarized in Table 1. The crystal diffracted rather weakly. Standard Patterson and difference Fourier approaches revealed all the non-hydrogen atoms; hydrogen atoms were fixed in calculated positions. Because of the relatively small number of data, only the rhenium atoms and the atoms coordinated to rhenium were refined anisotropically. All calculations used the SDP/VAX package of programs supplied by the Enraf-Nonius Corp., with scattering factors and anomalous dispersion terms taken from the standard compilation.[30]

Acknowledgment. We are grateful to the National Science Foundation and the DuPont Co. for financial support. We thank Dr. Sue C. Critchlow for her assistance with the X-ray crystallography and Drs. D. D. DuMez and W. S. McNeil for general assistance. S.N.B. acknowledges a National Science Foundation Predoctoral Fellowship, a Shell Graduate Fellowship, and a Howard J. Ringold Fellowship of the University of Washington Department of Chemistry.

Supporting Information Available: Tables of crystal data, atom positional and thermal parameters, and bond distances and angles for (HBpz$_3$)ReO(Ph)$_2$ (**5**) (8 pages). Ordering information and Internet access instructions are given on any current masthead page.

OM980216Y

---

[30] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974.