nonexpensive, commercial chemicals (H_2O_2, $NaNO_2$, H_2SO_4, and CH_3CN) and can be classified as a sulfoxidation reaction with "activated" H_2O_2. The activation consists of the fast reaction of H_2O_2 with HNO_2 in acidified CH_3CN to form the unstable, yet highly reactive, oxidant peroxynitrous acid ONOOH as an intermediate species in situ. The experimental conditions can be easily set in such a way that the reaction of the electrophile ONOOH with the nucleophile RSR′ is fast enough to compete successfully with the decay of ONOOH to nitric acid. Under these optimized conditions, HNO_2 acts as a catalyst, quickly carrying oxygen atoms from H_2O_2 to the sulfide in the form of ONOOH.

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[6] The use of commercial H_2O_2 as a reagent necessarily introduces some water into the system. The solvent acetonitrile with a constant admixture of water (5 M) was therefore taken as the standard reaction medium.

[7] The absorbance/time data shown in Figure 1 were obtained with a multi-wavelength stopped-flow spectrophotometer described earlier.[8] The absorptivity of ONOOH in the range 250–350 nm is greater than that of nitrous and nitric acid. The initial increase in absorbance A at 260 nm corresponds therefore to the formation of ONOOH, the consecutive decrease to its decay. The rate constants k_f and k_d were obtained from Equation (5) using the A/t data (a_1, a_2 = amplitudes).

$$A = a_1\exp(-k_f t) + a_2\exp(-k_d t) + A_\infty \qquad (5)$$

[8] C. Drexler, H. Elias, B. Fecher, K. J. Wannowius, *Fresenius J. Anal. Chem.* **1991**, *340*, 605–615.

[9] D. J. Benton, P. J. Moore, *J. Chem. Soc. A* **1970**, 3179–3182.

[10] Standard procedure and conditions: A solution of H_2O_2, H_2SO_4, and H_2O in CH_3CN (1 mL) was quickly mixed with a solution of the organic substrate A and $NaNO_2$ in CH_3CN (1 mL) to obtain the reaction mixture with $[H_2O_2] = 0.2\,\text{M}$, $[HNO_2] = 0–45\,\text{mM}$, $[A] = 0.5\,\text{M}$, $[H_2SO_4] = 0.08\,\text{M}$, and $[H_2O] = 5\,\text{M}$ (the pK_a of HNO_2 is 3.3; to liberate HNO_2 from $NaNO_2$, the condition $-\lg[H^+] < 3$ has to be fulfilled). The mixture was stirred at ambient temperature. At adequate time intervals, samples (0.2 mL) were taken and diluted with water for the cerimetric determination of H_2O_2.

[11] K. N. Houk, K. R. Condroski, W. A. Pryor, *J. Am. Chem. Soc.* **1996**, *118*, 13002–13006.

[12] The value of $k = (31 \pm 3) \times 10^{-4}\,\text{M}^{-1}\,\text{s}^{-1}$ (see Table 1) was obtained by fitting of the $[H_2O_2]/t$ data shown in Figure 2a to Equation 6. This

$$[H_2O_2] = [H_2O_2]_o \exp(-k[\text{PhSMe}]t) \qquad (6)$$

value is very close to $k = 37.3 \times 10^{-4}\,\text{M}^{-1}\,\text{s}^{-1}$ as reported for the sulfoxidation of PhSMe with H_2O_2 in EtOH (6% H_2O).[13]

[13] G. Modena, L. Maiola, *Gazz. Chim. Ital.* **1957**, *87*, 1306–1316.

[14] The reaction between Me_2S and ONOOH in water was recently shown to be second-order, first-order in both reactants.[3] The oxidation of organic sulfides by hydroperoxides is generally found to be a second-order process.[15]

[15] J. O. Edwards in *Peroxide Reaction Mechanisms* (Ed.: J. O. Edwards), Wiley-Interscience, New York, **1962**, pp. 67–106.

[16] It was confirmed by experiment that ONOOH, when generated according to Equation (1), does not decompose H_2O_2 according to the reaction $ONOOH + H_2O_2 \rightarrow HNO_2 + H_2O$.

[17] At the lowest Me_2S concentration, $[Me_2S] = 5\,\text{mM}$, almost half of the H_2O_2 is consumed for the fast Me_2S oxidation by ONOOH (see Figure 3). This means that the Me_2S concentration at which $k_{Me_2S}[Me_2S] = k_d$ is smaller than 5 mM and, hence, $k_{Me_2S} > 0.61/0.005 = 122\,\text{M}^{-1}\,\text{s}^{-1}$.

[18] GC analysis was carried out with an Auto System Gas Chromatograph with FI detector (Perkin-Elmer) and a 15-m capillary column (Alltech; Heliflex AT-1000) at 150 °C (Me_2S) and 170 °C (PhSMe). The samples were neutralized with NaOH before injection.

[19] Concentrated H_2SO_4 (1 mL, 98%) and technical grade, stabilized 35% H_2O_2 (4 mL, 47 mmol) were added to a well-stirred solution of $(PhCH_2)_2S$ (5.3 g, 25 mmol) in CH_3CN (250 mL) at ambient temperature. To start the fast catalyzed reaction, a solution of $NaNO_2$ (320 mg, 4.7 mmol) in water (2 mL) was added in one portion (**caution**: the reaction is exothermic! In the case of larger batches the reaction mixture should be efficiently thermostated). After a reaction time of five minutes the solution was set to pH 7 with a solution of NaOH (1 M) diluted with water (70 mL) and extracted with chloroform (3 × 130 mL). The chloroform phase was dried with $MgSO_4$ and taken to dryness in vacuo. The residue was recrystallized from EtOH. Yield: 5.1 g (91%). M.p. 133 °C (134–135 °C[20]). ^{1}H NMR and IR spectroscopy as well as C,H,N analysis proved the identity of the product as dibenzyl sulfoxide.

[20] *Handbook of Chemistry and Physics*, 51st ed., The Chemical Rubber Co. **1970–1971**.

Synthesis, Structure, and Reactivity of a Palladium Hydrazonato Complex: A New Type of Reductive Elimination Reaction To Form C–N Bonds and Catalytic Arylation of Benzophenone Hydrazone**

John F. Hartwig*

Reductive elimination reactions which form C–N bonds in amines[1–4] are important primary reactions in practical catalytic cycles for the synthesis of arylamines from aryl halides.[1, 5–8] Reductive elimination reactions that result in *N*-arylhydrazones would be an important new method for C–N bond formation by means of reductive elimination. The hydrazone products could be used in Fischer indole syntheses or, after conversion into the *N*-arylhydrazine, in condensation reactions to produce *N*-arylpyrazoles and *N*-arylpyrazolones.

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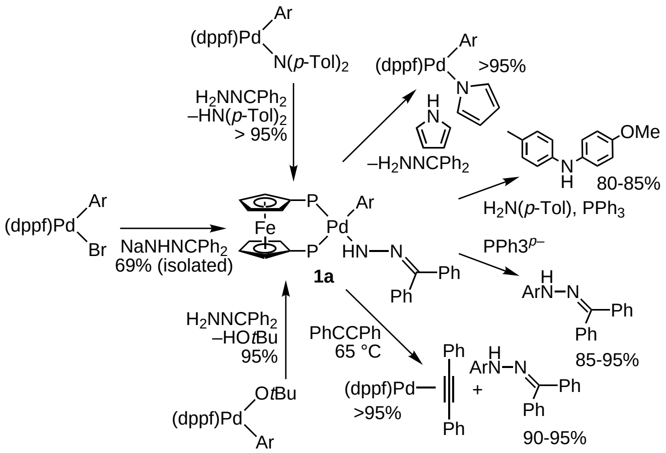
A large number of hydrazonato complexes have been prepared, but many display either μ^2[9] or η^2 coordination modes[10, 11] which lead to stable complexes. Here the first monomeric, η^1-hydrazonato complex characterized by X-ray diffraction is reported, together with reactions to evaluate its stability in comparison with related amido and pyrrolyl complexes. In addition, the reductive elimination of *N*-arylhydrazone, and the palladium-catalyzed arylation of a representative hydrazone are discussed.

The synthesis and reactivity of [Pd(dppf)(*p*-MeOC$_6$H$_4$)(NH−N=CPh$_2$)] (**1a**) are shown in Scheme 1. Reaction of NaNH−N=CPh$_2$ with [Pd(Br)(dppf)(*p*-MeOC$_6$H$_4$)] cleanly gave **1a**, which was isolated in 69% yield.[2] The ^{31}P NMR spectrum of **1a** shows two sharp doublets, demonstrating that DPPF remains chelated to the metal center, and that the complex is square planar in solution. The IR spectrum of **1a** showed a C=N band at 1575 cm^{-1}, which is consistent with an η^1 coordination mode since free diphenylhydrazone vibrates at 1571 cm^{-1}.



Scheme 1. Synthesis and reactions of [Pd(dppf)(Ar)(NH−N=CPh$_2$)] (**1a**). Ar = *p*-MeOC$_6$H$_4$, DPPF = 1,1′-bis(diphenylphosphanyl)ferrocene, Tol = tolyl.

An ORTEP drawing of a more crystalline analogue [Pd(dppf)(*o*-MeC$_6$H$_4$)(NH−N=CPh$_2$)] (**1b**)[12] is provided in Figure 1.[13] Complex **1b** is monomeric, square planar, and contains a terminal hydrazonato ligand. The sum of the four angles about the Pd center is 360.4°. The nitrogen atom in the position β to the Pd center lies nearly within the square plane, which precludes any formulation of the complex as a square-based pyramid; the distance between the Pd center and the second nitrogen atom is greater than 3 Å. No previous examples of simple η^1, μ^1 hydrazonato complexes were found in the Cambridge Crystallographic Database. The Pd1−N1 bond length of 2.035(9) Å is 0.06 Å shorter than that in the related DPPF-ligated palladium diarylamido complex.[2] The N1−N2 bond length of 1.35(1) Å in **1b** is shorter than the typical N−N bond lengths in hydrazones (1.38 – 1.41 Å),[14] but the C1=N2 bond of 1.32(1) Å is no longer than usual for hydrazones,[14] and the $\tilde{\nu}_{CN}$ value is not reduced from that for free diphenylhydrazone. The P1-Pd1-P2 angle of 99.8(1)° is roughly 1.5° smaller than the corresponding angle in the more sterically crowded diarylamido complex. The palladium-bound aryl group is twisted by 99° out of the palladium square plane, and this geometry, coupled with hindered rotation, gives rise to eight cyclopentadienyl resonances in the ^{1}H NMR spectrum.

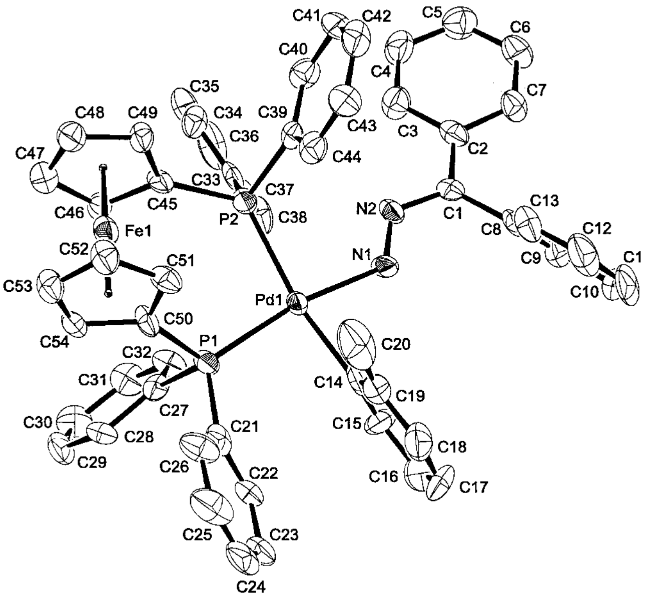


Figure 1. ORTEP drawing of **1b**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1−P1 2.293(3), Pd1−P2 2.374(4), Pd1−N1 2.035(9), Pd1−C14 2.03(1), N1−N2 1.35(1), N2−C1 1.32(1); P1-Pd1-P2 99.8(1), P1-Pd1-C14 88.9(3), P2-Pd1-N1 89.8(3), N1-Pd1-C14 81.9(4).

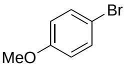
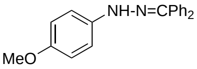
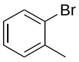
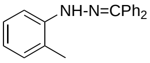
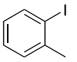
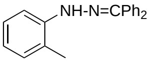
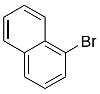
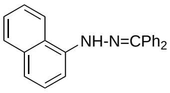
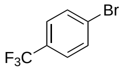
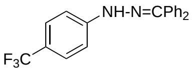
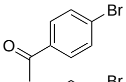
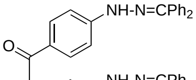
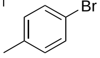
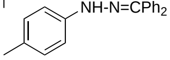
Scheme 1 includes reactions that result in **1a** upon exchange of the σ-bonded ligands. These simple exchange reactions were complete within 30 minutes at room temperature. Complex **1a** was generated in essentially quantitative yield by the reaction of benzophenone hydrazone with the diarylamido complex [Pd(dppf)(*p*-MeOC$_6$H$_4$){N(*p*-Tol)$_2$}].[2] The palladium alkoxide [Pd(dppf)(*p*-MeOC$_6$H$_4$)(O*t*Bu)][18] reacted with benzophenone hydrazone to form **1a** and *t*BuOH in a process that is similar to reactions with amine substrates.[15–17]

Reaction of **1a** with pyrrole generated the palladium pyrrolyl complex [Pd(dppf)(*p*-MeOC$_6$H$_4$)(NC$_4$H$_4$)].[19] Although treatment with toluidine did not afford the arylamido complex [Pd(dppf)(*p*-MeOC$_6$H$_4$)(NH-*p*-Tol)] in observable quantities, the mixture of **1a** and toluidine produced *p*-MeOC$_6$H$_4$NH-*p*-Tol in 80 – 85% yield after 12 h at room temperature. Thus, reaction of **1a** most likely forms small amounts of [Pd(dppf)(*p*-MeOC$_6$H$_4$)(NH-*p*-Tol)]; this complex is analogous to related complexes that eliminate diarylamines at room temperature.[1, 2] Overall, the stability of **1a** lies in the middle of the stability range for complexes known to undergo C−N bond formation by reductive elimination.

This data on relative stability suggests that **1a** should undergo reductive elimination to form C−N bonds. Indeed, when a solution of **1a** was warmed to 70 °C for 2 h with either PPh$_3$ or diphenylacetylene to trap the Pd^0 product, *N*-arylhydrazone was formed in greater than 85% yield, as determined by ^{1}H NMR spectroscopy with an internal standard. For reactions carried out in the presence of PPh$_3$, the Pd^0 products were a combination of [Pd(dppf)$_2$] and PPh_3 complexes of Pd^0.[20] For reactions with diphenylacetylene as the trapping reagent, [Pd(dppf)(PhCCPh)] was formed as the Pd^0 product. This compound was not isolated, but its identity was confirmed by independent synthesis from [Pd{P(*o*-Tol)$_3$}$_2$], DPPF (1 equiv), and PhCCPh (1 equiv). Quantitative rate studies showed that the reaction was first order in the palladium complex and zero order in trapping reagents. The k_{obs} values for reactions with 0.022 – 0.11 M [D_{15}]PPh_3 averaged 3.8×10^{-4} with an estimated standard deviation of only 0.4×10^{-4}, while the k_{obs} value for reactions with PhCCPh as the trapping reagent averaged $(3.7 \pm 0.1) \times 10^{-4}$. The lack of an influence of the concentration of the trapping reagent on the reaction rate has also been observed for other C–N bond-forming reductive elimination reactions from DPPF-ligated palladium complexes,[2] and suggests that the reductive elimination of **1a** follows a similar intramolecular elimination pathway.

These findings imply that one could produce *N*-arylhydrazones catalytically from aryl halides, inexpensive diphenylhydrazone, an alkoxide base, and a DPPF-ligated palladium complex. The results from such studies are summarized in Table 1. Electron-rich, electron-poor, sterically hindered, or unhindered aryl bromides or iodides all reacted with benzophenone hydrazone in the presence of a base and 1 mol% of a palladium complex formed in situ from [Pd(OAc)$_2$] and DPPF or 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl (BINAP). Cesium carbonate was an effective base for these reactions, so that even base-sensitive functionalities on the aryl halide could be tolerated.[21] For example, entry 7 shows that the use of DPPF as a ligand enabled cesium carbonate to be used as a base for aryl halide substrates that are not electron-poor. No competing diarylation[8, 22] of the hydrazone was observed in the reactions in Table 1, and only trace amounts of diphenylmethane (<2%), possibly generated from Wolf – Kischner reduction,[23] were detected.

Table 1. Palladium-catalyzed arylation of diphenylhydrazone.[a]

Entry	Substrate	Ligand	Base	Product[b]	Yield [%][c]
1		BINAP	NaO*t*Bu		80
2		DPPF	NaO*t*Bu		99
3		DPPF	NaO*t*Bu		91
4		DPPF	NaO*t*Bu		86
5		DPPF	Cs_2CO_3		91
6		DPPF	Cs_2CO_3		96
7		DPPF	Cs_2CO_3		86

[a] All reactions were run with 1 mol% [Pd(OAc)$_2$], 1.5 mol% ligand, 1.5 equiv of base, 1.2 equiv of diphenylhydrazone, and 1.0 mmol of substrate. The reactions in entries 1 – 6 were run for 8 h at 90 °C with 2 mL of toluene as solvent. The reaction in entry 7 was run for 12 h at 100 °C with 0.5 mL of toluene as solvent. [b] All isolated products were judged pure by ^1H and ^{13}C NMR spectroscopy and GC analysis. New compounds in entries 4 – 6 were also characterized by elemental analysis. The product in entry 1 discolored upon standing at room temperature and was analyzed by HR-MS. Products in entries 2, 3, and 7 have been prepared previously.[24] [c] Yield of the isolated product.

In conclusion, this work demonstrates that an η^1-hydrazone is a viable intermediate in reductive elimination reactions to form C–N bonds in palladium-catalyzed arylation chemistry. This complex is more stable than the related amido derivatives, both thermally and toward proton transfer. Nevertheless, the reductive elimination process occurs in high yields at mild temperatures. The stronger acidity of the hydrazone relative to amines and arylamines allows the catalytic reaction to be carried out with simple ligands and a carbonate base.[25]

Experimental Section

1: Solid $NaNHNCPh_2$ (33 mg, 0.15 mmol) was added with stirring to a slurry of [Pd(I)(dppf)(*p*-$MeOC_6H_4$)] (90 mg, 0.10 mmol) in THF (2 mL). This mixture was stirred for 5 min, during which time the solution became orange and the solid starting complex was consumed. The solvent was removed under reduced pressure, and the resulting solid was extracted with toluene (5 mL). The toluene extract was filtered through celite, the volume was reduced by half, and pentane was layered onto the solution. After the mixture was cooled at −35 °C for 12 h, 66 mg (69% yield) of orange **1** were isolated by removal of the supernatant with a pipette and washing of the solid with pentane. ^1H NMR (300 MHz, [D_6]benzene, 25 °C, TMS): $\delta = 8.51$ (pseudo t, $J = 8.3$ Hz, 4H), 7.54 (dd, $J = 8.7, 11.0$ Hz, 4H), 6.8 – 7.3 (m, 25H), 6.44 (d, $^3J_{H,H} = 7.1$ Hz, 2H), 4.60 (d, $^3J_{H,H} = 1.7$ Hz, 2H), 4.00 (s, 2H), 3.79 (s, 2H), 3.76 (s, 2H), 3.37 (s, 3H); $^{31}P\{^1H\}$ NMR (122 MHz, [D_6]benzene, 25 °C, 85% H_3PO_4): $\delta = 27.52$ (d, $^2J_{P,P} = 30.5$ Hz), 13.83 (d, $^2J_{P,P} = 30.5$ Hz); IR(Nujol): $\tilde{\nu}_{N-H} = 3228$, $\tilde{\nu}_{C=N} = 1575\ cm^{-1}$; elemental analysis calcd for $C_{54}H_{46}FeN_2OP_2Pd \cdot C_7H_8$: C 69.43, H 5.16, N 2.65; found: C 69.65, H 5.19, N 2.45.

Hydrazone arylation: [Pd(OAc)$_2$] (2.2 mg, 0.01 mmol), DPPF or BINAP (0.015 mmol), NaO*t*Bu or Cs_2CO_3 (1.5 mmol), and benzophenone hydrazone (235 mg, 1.2 mmol) were placed into a screw-capped vial with a stir bar. An aryl halide (1.0 mmol) was placed into a separate vial and dissolved in toluene (0.5 – 2.0 mL). The solution was then transferred to the screw-capped vial. The vial was sealed with a cap containing a teflon-lined septum and then placed in an oil bath (90 or 100 °C). GC/MS analysis of the reaction mixture showed complete consumption of the aryl halide after 12 h. The reaction mixture was filtered, the solid was washed with ethyl acetate, and the solvent was removed under reduced pressure. The resulting oil was purified by chromatography (silica gel, elution with hexane/ethyl acetate).

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[12] This complex was prepared in a similar fashion to **1a**. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25°C, TMS): $\delta = 8.52$ (pseudo q, $J = 9$ Hz, 4H), 7.88 (m, 4H), 6.65–7.45 (m, 25H), 6.44 (d, $^3J_{\mathrm{H,H}} = 7.2$ Hz, 2H), 4.98 (br s, 1H), 4.23 (s, 1H), 4.09 (s, 1H), 3.96 (s, 1H), 3.93 (s, 1H), 3.78 (s, 1H), 3.73 (s, 1H), 3.68 (s, 1H), 2.66 (s, 3H); in addition, a ratio of 0.5 toluene molecules per **1b** molecule was determined; ^{31}P{^{1}H} NMR (122 MHz, [D$_6$]benzene, 25°C, 85% H_3PO_4): $\delta = 27.22$ (d, $^2J_{\mathrm{P,P}} = 30.6$ Hz), 13.97 (d $^2J_{\mathrm{P,P}} = 30.6$ Hz); IR(Nujol) $\tilde{\nu}_{\mathrm{N-H}} = 3224$, $\tilde{\nu}_{\mathrm{C=N}} = 1571$, 1594 cm^{-1}.

[13] Crystal structure analysis of **1b**: space group $P\bar{1}$ (no. 2), $a = 13.36(1)$, $b = 18.30(2)$, $c = 10.04(1)$ Å, $\alpha = 103.26(9)$, $\beta = 91.85(9)$, $\gamma = 78.32(8)°$, $V = 2339(4)$ Å^3, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.39$ g cm^{-3}, $2\theta_{\mathrm{max}} = 50.0°$, Mo$_{K\alpha}$ ($\lambda = 0.71069$ Å), $\omega - 2\theta$, 8.0° min^{-1} (in ω), $(1.26 + 0.3\tan\theta)°$, −105°C, 8616 reflections with 8231 unique. The data were corrected for Lorentz and polarization factors. No absorption correction was applied. The structure was solved by direct methods and refined with Fourier techniques and teXan software. Number of observations ($I > 3.00\sigma(I)$) 3147 and number of variables 577. H atoms were included but not refined. $R = 0.056$, $wR = 0.64$, refined against $|F|$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101249. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Spectra, Structure, Ligand Exchange, and Decomposition of a Tungsten(II) Ether Complex[**]

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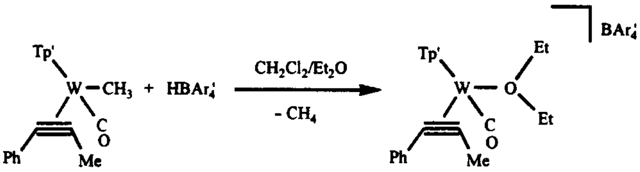
Ether ligands can reversibly bind to Lewis acidic metal moieties and thus stabilize reactive metal fragments and provide useful precursors for catalysts.[1–6] Ether complexes of the Group 6 elements[6–11] have been prepared from alkylidene complexes[7, 8] and by protonation of [WCp*(CO)$_3$(Me)] (Cp* = C_5Me_5) with HBAr$'_4$ in Et_2O.[9, 10] Addition of acid to [WCp(H)(CO)$_3$] (Cp = C_5H_5) and benzaldehyde dimethyl acetal gives the ether complex [WCp(CO)$_3$(PhCH$_2$OMe)][X] (X = $CF_3SO_3^-$, BAr$'_4$; Ar$'$ = 3,5-bis(trifluoromethyl)phenyl).[11] The synthesis of diethyl ether and dimethyl ether complexes of rhenium is also pertinent.[12]

We have now synthesized [WTp$'$(CO)(OEt$_2$)(PhC≡CMe)][BAr$'_4$] (**1**; Tp$'$ = hydridotris(3,5-dimethylpyrazol-1-yl)borate). To determine whether **1** is a convenient precursor for the reactive fragment [WTp$'$(CO)(PhC≡CMe)]$^+$,[13] we studied the substitution of the labile ether ligand by acetonitrile and the decomposition of **1** in dichloromethane.

Reaction of [WMeTp$'$(CO)(PhC≡CMe)][14] with HBAr$'_4$ in CH_2Cl_2/Et_2O (ca. 2/1) yields **1** in 70% yield [Eq. (a)].



1

(a)

Formation of **1** is accompanied by a color change from dark blue to light blue, and the CO stretching frequency increases from 1875 to 1923 cm^{-1}. Complex **1** is stable for days at room temperature in dichloromethane in the presence of an excess of diethyl ether. However, if no excess of diethyl ether is present, **1** decomposes rapidly (ca. 2 h, see below). In the solid state, **1** is stable for weeks in air and indefinitely under an inert atmosphere.

The ^{1}H NMR spectrum of **1** in CD_2Cl_2 at −80°C reflects restricted rotation about the tungsten–ether bond. Thus, four multiplets are observed for the four methylene protons of the ether ligand in the range $\delta = 3-5$. Each multiplet consists of five lines, and this is consistent with nearly equal geminal and vicinal coupling constants ($^2J_{\mathrm{HH}} \approx {}^3J_{\mathrm{HH}} \approx 7$ Hz). Two triplets are observed for the methyl groups of the coordinated ether. The ^{13}C NMR spectrum (−80°C) displays typical resonances for the ligands (alkyne as four-electron donor) and the

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