

complex, occurs within the potential limits of an aqueous solution. (The  $H_n$  notation in the formula indicates the number of amidate nitrogens coordinated to the palladium.) Flow electrolysis of pale yellow **1** at 1.35 V vs. Ag/AgCl produces a pink species, **2**. The CV behavior of **2** is very similar to that of **1**. Typically, flow electrolysis of 1–2 mM solutions of **1** proceeds with >90% yield. The oxidized species, **2**, in 0.050 M chloroacetate buffer, pH 3.0, with 0.10 M NaCl undergoes an absorbance loss of only 15% in 1 h when protected from room light. The products of the thermal decay in aqueous solution are palladium(II) species, as determined by UV-vis spectroscopy. In acetonitrile the stability of **2** is excellent, with <1% loss in 1 h when protected from room light.

The following experimental facts indicate oxidation of **1** occurs at the metal center and that **2** is formally a palladium(IV) species.

1. Reaction of **2** with the two-electron reductant iodide to give  $I_3^-$  or with the one-electron reductant  $[Cu(H_2Aib_3)]^-$  to give  $Cu(H_2Aib_3)$  shows that **2** is 2 equiv more oxidized than **1**.

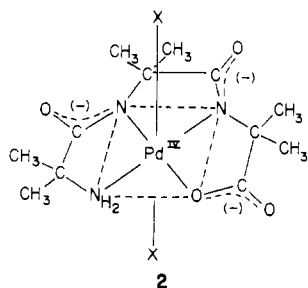
2. In aqueous solution **2** is EPR silent at 77 K but NMR active at room temperature, consistent with the metal-centered oxidation of  $d^8$  palladium(II) to  $d^6$  palladium(IV). A comparison of the  $^1H$  NMR spectral data for  $H_2Aib_3^+$ , **1**, and **2** in Table I suggests a metal-centered oxidation with a more electron-withdrawing metal coordinated to the ligand in **2** than in **1**.

3. The chemical oxidation of **1** to **2** with Oxone ( $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ ) and the subsequent reduction of **2** to **1** with  $NH_2OH$  yields **1** in 95% yield. Thus, the conversion of **1** to **2** is reversible. Ligand-centered oxidation of **1** by Oxone in an aqueous solution with subsequent reduction would be expected to give a much lower yield of **1**.

4. The electronic spectral data for **2** collected in Table I show charge-transfer bands (presumably ligand-to-metal charge transfer (LMCT)) at longer wavelengths than those for **1**, as expected for an increase in the oxidation state of the central metal.

5. Visible radiation photoreduces the central metal in **2**. Divalent **1** is not subject to decomposition by visible radiation. Photoactivity appears to be a general characteristic of high-valent metal-amidate complexes since  $Cu(H_2Aib_3)^{13}$  and  $Ni(H_2Aib_3)^{5c}$  complexes are also photoactive for LMCT band irradiation.

The electronic spectral data for **2** under varying medium conditions as presented in Table I suggest axial halide coordination at low pH and axial hydroxide coordination at neutral pH. That is, the 243-nm LMCT shifts to 266 nm when the medium is changed from 0.10 M NaCl to 0.10 M NaBr; also, at pH 7 the spectrum is independent of the presence or absence of chloride. Since palladium(IV) is a  $d^6$  metal ion, an octahedral coordination geometry is expected. Thus we suggest a structure for **2** is  $[Pd(H_2Aib_3)_2X_2]^-$  where  $X = Cl^-$ ,  $Br^-$ , or  $OH^-$  depending on medium conditions.



Because of our success in the ready preparation of **2** without an excess of strong oxidant, we are able to begin investigation of the scope of reactivity of the palladium(IV) complex toward organic substrates. Our preliminary findings are (1) **2** in 0.050 M chloroacetate, pH 3.0, with 0.10 M NaCl oxidizes 2-butanol to 2-butanone in 60% yield and (2) carbon monoxide reacts rapidly

with **2** in a redox reaction that initially produces **1** quantitatively. The fate of the carbon monoxide has not yet been determined. Control experiments show that **1** does not react with either 2-butanol or carbon monoxide in the same time period. These preliminary reactivity data encourage us to further examine the range of substrates with which the palladium(IV) species will react. For instance, oxidative-addition reactions with palladium(II)-amidate complexes should also be possible since we have shown in this report that palladium(IV) is an accessible and reasonably stable oxidation state with multidentate amide ligands.

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**Registry No.** **1**, 96928-70-0; **2** ( $X = Cl$ ), 96914-29-3; **2** ( $X = Br$ ), 96914-30-6; **2** ( $X = OH$ ), 96914-31-7;  $H_2Aib_3^+$ , 96914-32-8; CO, 630-08-0;  $NH_2OH$ , 7803-49-8; 2-butanol, 78-92-2; 2-butanone, 78-93-3; Oxone, 37222-66-5.

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### Preparation and Protonation of $[ReBr_2(N_2Ph)_2(PPh_3)_2]$ . Structure of $[ReBr_2(NNPh)(NNHPh)(PPh_3)_2]$ , a Complex with a Hydrazido(2-) Ligand with a Large Angular Distortion

Sir:

Although there have been extensive studies of mono(diazenido) complexes,<sup>1</sup> there are relatively few reports of the chemistry and properties of complexes containing two diazenido ligands.<sup>2</sup> Here we describe the synthesis and protonation of the first bis(diazenido) complex of rhenium. Shortly after the structural work was complete, we became aware of the more extensive studies by Haymore.

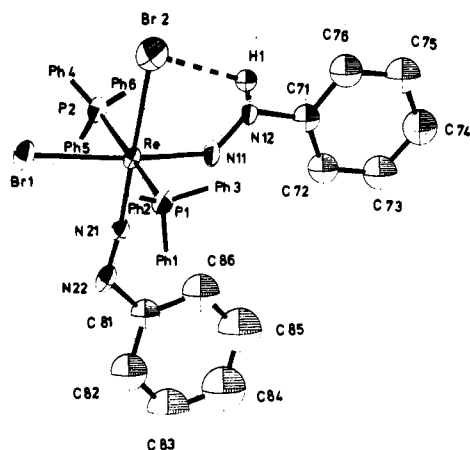
We therefore restrict ourselves here to a description of our different synthetic method and of an X-ray crystal structure analysis of a complex with a highly bent hydrazido(2-) ligand.

The most frequently employed synthetic routes to aryldiazenido complexes involve oxidative addition of a diazonium salt or insertion into a metal-hydrogen bond to give a diazene complex that is subsequently deprotonated. The silylated diazene  $Me_3SiN_2Ph$  has been used much less frequently<sup>3,4</sup> but provides a very efficient way of introducing the aryldiazenido function. The rhenium(V)-oxo complex  $[ReOCl_3(PPh_3)_2]$  reacts with 4 equiv of  $Me_3SiN_2Ph$  in dry dichloromethane to give  $[ReCl(N_2Ph)_2(PPh_3)_2]$  (**I**) as a pale orange precipitate in about 70–80% yield. There is slow evolution of dinitrogen, and the silyldiazenide functions as a reducing agent. The bromo analogue of **I** is made analogously from  $[ReOBr_3(PPh_3)_2]$ .

Both complexes show strong infrared bands at about 1550 and 1510  $cm^{-1}$  assigned to  $\nu(N=N)$ . The complexes are only very sparingly soluble in organic solvents, which precluded solution

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**Figure 1.** ORTEP view of the structure of  $[\text{ReBr}_2(\text{N}_2\text{Ph})(\text{NNHPh})(\text{PPh}_3)_2]$  showing the atom-labeling scheme. Selected bond lengths (Å) and angles (deg): Re–Br1, 2.600 (2); Re–Br2, 2.592 (2); Re–P1, 2.477 (5); Re–P2, 2.481 (5); Re–N11, 1.922 (11); Re–N21, 1.793 (11); N11–N12, 1.287 (15); N21–N22, 1.212 (16); N12–Br2, 3.047; H1–Br2, 2.471; Br2–Re–Br1, 90.1; P1–Re–Br1, 87.8 (1); P1–Re–Br2, 90.3 (1); P2–Re–Br1, 89.5 (1); P2–Re–Br2, 87.4 (1); P2–Re–P1, 176.4 (1); N11–Re–Br1, 175.0 (4); N21–Re–Br2, 177.3 (5); N12–N11–Re, 131.2 (10); N11–N12–C71, 120.6 (11); N22–N21–Re, 172.4 (10); N21–N22–C81, 120.2 (11); Br2...H1–N12, 123.7.

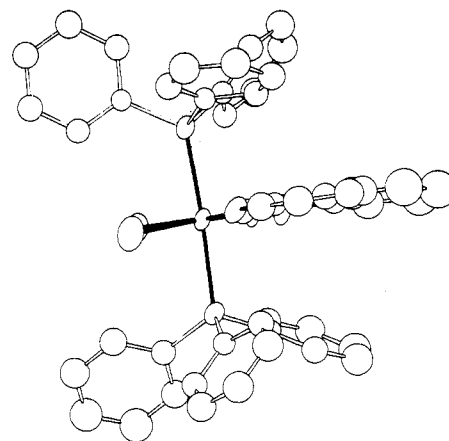
measurements of molecular weight or NMR spectra. However the lack of solubility suggests the complexes may be dimeric with chloride bridges and preliminary X-ray diffraction studies of a crystal that decomposed in the beam certainly support this postulate. The formation of a halogen-bridged structure requires one of the diazenido ligands to be doubly bent for the metal to conform to the 18-electron rule. However the observed infrared spectra are not sufficient to determine the geometry of the diazenido ligands.

Complex I reacts with an excess of HCl in methanol to give orange  $[\text{ReCl}_2(\text{N}_2\text{HPh})(\text{N}_2\text{Ph})(\text{PPh}_3)_2]$  (II) and with an excess of HBr to give orange  $[\text{ReBr}_2(\text{NNHPh})(\text{N}_2\text{Ph})(\text{PPh}_3)_2]$  (III). Complex I loses all chloride ions on reaction with an excess of HBr to give the dibromo complex III. These complexes show two strong characteristic infrared bands at about 1570 and 1320  $\text{cm}^{-1}$  with a medium-intensity band at 1620  $\text{cm}^{-1}$ . There are no infrared bands in the 3000–3500- $\text{cm}^{-1}$  region assignable to  $\nu(\text{N}-\text{H})$ . However a peak at 12.3 ppm in the  $^1\text{H}$  NMR spectrum was assigned to a hydrogen bound to a diazenido ligand. The observed spectroscopic properties are not sufficient to distinguish between the two possible protonation sites on the diazenido ligand, and accordingly an X-ray crystal structure analysis of III was undertaken.

**Crystal Data:** Triclinic, space group  $P\bar{1}$  with  $a = 12.133$  (6) Å,  $b = 12.317$  (5) Å,  $c = 16.245$  (6) Å,  $\alpha = 105.89$  (3)°,  $\beta = 103.38$  (3)°,  $\gamma = 71.64$  (3)°,  $V = 2187.9$  Å<sup>3</sup>,  $Z = 2$ . The structure is based on 4804 reflections with  $I > 3\sigma(I_0)$ , the final  $R$  value being 0.068.

An ORTEP view of the structure is shown in Figure 1, which also shows the atom-labeling scheme. The overall geometry about the rhenium is pseudooctahedral with trans triphenylphosphine ligands. The bromide ligands are cis, and one of the remaining coordination positions is occupied by a linear phenyldiazenido ligand (nitrogens N21, N22). The bond lengths in this ligand lie within the normal range (Re–N21 = 1.793 (11) Å; N21–N22 = 1.21 Å) found for phenyldiazenido complexes. The ligand has an essentially linear Re–N–N system and it is bent at N22, suggesting it is functioning as a formal 3-electron donor to the metal.

The other nitrogen ligand containing N11 and N12 is protonated at N12, H1 being located directly from the electron-density map. The ligand is therefore formally a hydrazido(2–) ligand. However, unlike the majority of such complexes, the ligand is drastically bent at N11 with Re–N11–N12 = 131.2 (10)°. This bending at N11 is the largest yet reported, the closest being that



**Figure 2.** ORTEP view of  $[\text{ReBr}_2(\text{NNHPh})(\text{N}_2\text{Ph})(\text{PPh}_3)_2]$  showing the coplanarity of the hydrazido(2–) and diazenido ligands. Atom numbering is omitted for clarity.

in  $[\text{W}(\eta^5\text{-C}_5\text{H}_5)\text{H}(\text{NNHPh})]^+$ , which is 138°. The geometry is explicable in terms of the 18-electron rule. For the ligand to be linear and function as a 4-electron donor, the metal would have a 20-electron count. The alternative way of achieving 18 electrons, by bending at N21 so that the normally 3-electron-donor diazenido ligand becomes a bent 1-electron donor, is not adopted. The absence of any electron density about N22 ascribable to a hydrogen (in contrast to N12) rules out the interpretation that the N21–N22 ligand is actually a hydrazido(2–) ligand protonated at N22 and that the N11–N12 ligand is a “doubly bent” diazenido ligand. The bond distances in the hydrazido(2–) ligand are generally very similar to those in  $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2\text{H}(\text{NNHPh})]^+$ .<sup>5</sup>

In principle, protonation of the diazenido ligand could have occurred at N11 to give phenyldiazeno. Similar reactions are well-known for diazenido complexes of the platinum group metals. However in complex III the presence of a hydrogen bond between H1 and Br2 favors protonation occurring at N12 rather than N11. The chloro analogue II has been shown to be essentially isostructural with III, the hydrogen bonding pattern being retained. Details of this structure will be reported elsewhere.

A least-squares-plane analysis shows that atoms Re, Br2, N11, N12, N21, N22, H1, and the two phenyl rings shown in Figure 1 are essentially coplanar. The planarity of the nitrogen ligand systems is clearly shown in Figure 2. This suggests that there may be delocalization throughout the Ph–N=N–Re=N–NHPh system.

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**Registry No.** I, 96913-76-7; II, 96913-77-8; III, 96913-78-9;  $[\text{ReBr}(\text{N}_2\text{Ph})_2(\text{PPh}_3)_2]$ , 96913-79-0;  $[\text{ReOBr}_3(\text{PPh}_3)_2]$ , 18703-07-6;  $[\text{ReOCl}_3(\text{PPh}_3)_2]$ , 17442-18-1.

**Supplementary Material Available:** Positional and thermal parameters for  $[\text{ReBr}_2(\text{N}_2\text{Ph})_2(\text{PPh}_3)_2]$  (2 pages). Ordering information is given on any current masthead page.

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