Similar studies[22] in which (4,11-CT)$Co(OH)(OH_2)^{2+}$ (4,11-CT = Me_6[14]diene(4,11)N_4) was added to preformed β,γ-$(tn)_2CoATP^-$ led to no observable enhancements in rates of P_i production (except for the very slight enhancements characteristic for the latter complex alone). In (4,11-CT)$Co(OH)(OH_2)^{2+}$ the water and hydroxide are exclusively trans to one another. The additional P_i, formed after OH^- quenching, can arise through a conventional S_N1CB mechanism[6] in which ring opening of a diphosphate chelate (in VI, VII, and VIII) or loss of a monodentate coordinated phosphate (in V) provide cis-coordinated hydroxide. A preference for trans geometry following the initial Co–O cleavage would explain the low yields of additional P_i where the $(tn)_2Co^{III}$ moiety is involved.[23] The latter aspects are under continued study.

The present studies, augmenting earlier findings from several laboratories, provide a clear demonstration of mechanistic features that should be of general importance in the promotion or inhibition of phosphoryl-transfer reactions by aquo metal ions: these include the requirement of cis-coordinated OH^- for high reactivity in the middle pH region,[3,5–7] the importance of cis/trans isomerism at the metal center,[6b–d,7] the importance of complexes containing more than one metal ion for effective promotion of polyphosphate hydrolysis,[3–5,6d,7] and the property of low reactivity for complexes in which all constituent metal ions are saturated by full chelation.[4,5,6d,8] Especially noteworthy, for the present systems, are the high initial rates for P_i production on addition of trpnCo$(OH)(OH_2)^{2+}$ to β,γ-$N_4Co^{III}ATP^-$, the marked falloff in rates attributable to competitive reactions in which the added aquo metal ions become saturated by full chelation, and demonstration of the advantages of the Eu^{2+} quenching method for release of phosphate species coordinated to cobalt(III). The mechanistic features displayed have relevance to enzyme-promoted phosphoryl-transfer and related processes with metal ion requirements; here additional steric constraints imposed by the enzyme system may be expected to have marked influences on isomeric possibilities for metal complexes and hence on the manner in which metal ions and coordinated nucleophiles can participate.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. ATP, 56-65-5; trpnCo$(OH)(OH_2)^{2+}$, 96914-52-2; $(tn)_2CoATP^-$, 96914-53-3; trpnCo^{III}(aq), 96914-54-4; $(tn)_2Co^{III}$(aq), 89921-37-9; trpnCoATP⁻, 96914-55-5.

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[22] Tafesse, F.; Milburn, R. M., unpublished results.

[23] From Figure 1B one can see that quenching with OH^- produces only 1–2% additional P_i, with this amount independent of the quenching time.

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Received January 25, 1985

Characterization of an Easily Obtainable Palladium(IV)–Amidate Complex

Sir:

Transient palladium(IV) intermediates have been invoked to explain certain palladium-catalyzed transformations of organic compounds;[1] however, the paucity of palladium(IV) complexes with adequate stability in solution has hampered a detailed study of palladium(IV) chemistry.[2–4] Here we report on the electrochemical preparation of a palladium(IV)–amidate complex that has sufficient stability in the absence of other strong oxidants in aqueous and nonaqueous solvents for the ready characterization of its properties and for the sampling of its reactivity.

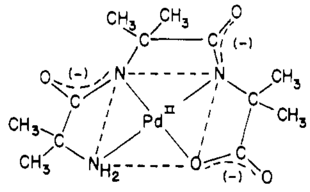
Table I. Spectral Data for Palladium(II, IV)–Aib_3 Complexes

species	medium conditions	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	^1H NMR[a] δ_{CH_3}
$H_2Aib_3^+$	"pH" = 3[b]	<210	1.41 1.25 1.24
1	0.10 M NaClO$_4$	<250 292 (1400)	1.30 1.20 1.11
2	0.10 M NaCl[c]	243 (27 500) 300 (7500) sh 390 (1500) sh 494 (660)	1.53 1.47 1.32
2	0.10 M NaBr[c]	266 310 sh 405 sh 522	
2	0.10 M NaCl[d] or NaClO$_4$[d]	233 sh 275 sh 430 sh	

[a] D_2O solution. [b] The "pH" of a D_2O solution. [c] 0.050 M chloroacetate, pH 3.0. [d] 0.050 M phosphate, pH 7.0.

The ligand system that stabilizes the palladium(IV) state is the tripeptide of α-aminoisobutyric acid, H–$[NHC(CH_3)_2CO]_3$–OH, $HAib_3$. The donor atoms responsible for this stabilization are anionic deprotonated amide nitrogens, i.e. amidate nitrogens. Multidentate ligands with amidate nitrogen donors have been used to characterize uncommon, high-valent states for other transition metals, e.g. copper(III),[5] nickel(III),[5c] silver(III),[6] osmium(VI),[7] and cobalt(IV)[8].

Cyclic voltammetry indicates that the electrochemical oxidation of $[Pd(H_{-2}Aib_3)]^-$[9] (**1**), the precursor to the palladium(IV)



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[1] (a) Ng, F. T. T.; Henry, P. M. *J. Org. Chem.* **1973**, *38*, 3338–3343. (b) Ito, T.; Tsuchiya, H.; Yamamato, A. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1319–1327. (c) Moravskiy, A.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4182–4186. (d) Uson, R.; Fornies, J.; Navarro, R. *J. Organomet. Chem.* **1975**, *96*, 307–312.

[2] Gulliver, D. J.; Levason, W. *Coord. Chem. Rev.* **1982**, *46*, 1–127.

[3] Gulliver, D. J.; Levason, W. *J. Chem. Soc., Dalton Trans.* **1982**, 1895–1898.

[4] Gray, L. R.; Gulliver, D. J.; Levason, W.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1983**, 133–141.

[5] (a) Birker, P. J. M. W. L. *Inorg. Chem.* **1977**, *16*, 2478–2482. (b) Bour, J. J.; Birker, P. J. M. W. L.; Steggerda, J. J. *Inorg. Chem.* **1971**, *10*, 1202–1205. (c) Kirksey, S. T., Jr.; Neubecker, T. A.; Margerum, D. W. *J. Am. Chem. Soc.* **1979**, *101*, 1631–1633.

[6] Kirschenbaum, L. J.; Rush, J. D. *J. Am. Chem. Soc.* **1984**, *106*, 1003–1010.

[7] (a) Christie, J. A.; Collins, T. J.; Krafft, T. E.; Santarsiero, B. D.; Spies, G. H. *J. Chem. Soc., Chem. Commun.* **1984**, 198–199. (b) Anson, F. C.; Christie, J. A.; Collins, T. J.; Coots, R. J.; Furutani, T. T.; Gipson, S. L.; Keech, J. T.; Krafft, T. E.; Santarsiero, B. D.; Spies, G. H. *J. Am. Chem. Soc.* **1984**, *106*, 4460–4472.

[8] Anson, F. C.; Collins, T. J.; Coats, R. J.; Gipson, S. L.; Richmond, T. G. *J. Am. Chem. Soc.* **1984**, *106*, 5037–5038.

[9] **1** was prepared by combining aqueous solutions of $HAib_3$ (10% excess) and $[PdCl_4]^{2-}$, slowly raising the pH to 7, and stirring at room temperature for several hours. After this time the spectrum for $[PdCl_4]^{2-}$ disappeared, and the spectrum for fully formed **1** was obtained. Circular dichroism[10,11] and UV–vis[10,12] spectral measurements and potentiometric titration[10] have shown that the absorption at 292 nm (see Table I) is characteristic of palladium(II)–tripeptide complexes in solution when the central metal ion is coordinated by an amine nitrogen, two amidate nitrogens, and a carboxylate oxygen. ^1H NMR spectra were collected on a Varian FT-80 instrument. The EPR spectra were recorded on a Varian E-3 spectrometer. Electronic spectra were obtained on a Perkin-Elmer Model 330 UV-VIS-NIR spectrophotometer.

[10] Wilson, E. W., Jr.; Martin, R. B. *Inorg. Chem.* **1970**, *9*, 528–532.

0020-1669/85/1324-2593$01.50/0

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 $[Cu(H_{-2}Aib_3)]^-$ to give $Cu(H_{-2}Aib_3)$ shows that **2** is 2 equiv more oxidized than **1**.

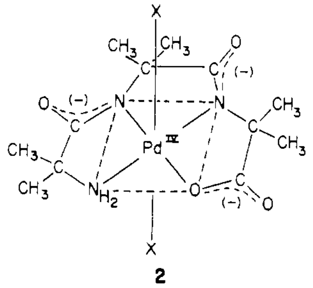
2. In aqueous solution **2** is EPR silent at 77 K but NMR active at room temperature, consistent with the metal-centered oxidation of d^8 palladium(II) to d^6 palladium(IV). A comparison of the ^1H NMR spectral data for $H_2Aib_3^+$, **1**, and **2** in Table I suggests a metal-centered oxidation with 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 $Cu(H_{-2}Aib_3)$[13] and $Ni(H_{-2}Aib_3)$[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 $[Pd(H_{-2}Aib_3)X_2]^-$ where X = Cl^-, Br^-, or OH^- depending on medium conditions.



2

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.

Acknowledgment. The authors wish to acknowledge financial support from an Atlantic Richfield Foundation Grant of the Research Corp. and a Research Initiation Grant of the University of Houston. The assistance of Mr. Haiwon Lee in obtaining the EPR spectrum is appreciated.

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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Received December 4, 1984

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(11) Cooper, J. C.; Wong, L. F.; Margerum, D. W. *Inorg. Chem.* **1978**, *17*, 261–266.
(12) Pitner, T. P.; Wilson, E. W., Jr.; Martin, R. B. *Inorg. Chem.* **1972**, *11*, 738–742.
(13) Hamburg, A. W.; Margerum, D. W. *Inorg. Chem.* **1983**, *22*, 3884–3893.

Preparation and Protonation of $[ReBr(N_2Ph)_2(PPh_3)_2]$. 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,[1] there are relatively few reports of the chemistry and properties of complexes containing two diazenido ligands.[2] 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[3,4] 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 silyldiazene 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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(1) Sutton, D. *Chem. Soc. Rev.* **1975**, 443.
(2) McCleverty, J. A.; Seddon, D.; Whitely, R. N. *J. Chem. Soc., Dalton Trans.* **1975**, 839. Carroll, W. E.; Deane, M. E.; Lalor, F. J. *J. Chem. Soc., Dalton Trans.* **1974**, 1837. Chatt, J.; Dilworth, J. R.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1979**, 1843. Colin, J.; Butler, G.; Weiss, J. *Inorg. Chem.* **1980**, 3828.
(3) Abel, E. W.; Burton, C. A.; Churchill, M. R.; Lin, K. K. G. *J. Chem. Soc., Chem. Commun.* **1974**, 268.
(4) Dilworth, J. R.; de Liefde Meyer, H. J.; Teuben, J. H. *J. Organomet. Chem.* **1978**, *159*, 47.

0020-1669/85/1324-2594$01.50/0