lished that pure **3** is transformed into **4** under these reaction conditions.[4]

Red, crystalline **3** exhibited two doublets in the $^{31}P\{H\}$ NMR spectrum ($CDCl_3$) at δ 212 and 79 (J = 43 Hz) and a metal hydride absorption in the ^1H NMR spectrum ($CDCl_3$) at δ −12.45 (dd, J = 45.0, 12.8 Hz). Its structure was established by X-ray crystallography and is shown as an ORTEP plot in Figure 1.[4] The Mo–Mo distance of 3.282 (1) Å is in the range expected for a single bond[5] and corresponds closely to that in $(\mu\text{-}PMe_2)(\mu\text{-}H)(\eta^5\text{-}Cp)_2(CO)_4Mo_2$, 3.26 Å.[6] The data were of sufficient quality[7] that the bridging hydrogen atom position was located and refined, but its unsymmetrical binding must be viewed with caution.[8]

Deep-green **4** featured a single absorption in the carbonyl stretching region (1710 cm^{-1}, CH_2Cl_2 solution) and a sharp singlet at δ 185 in the $^{31}P\{H\}$ NMR spectrum. The results of an X-ray structure determination on **4** are shown in an ORTEP plot (Figure 2).[4] The Mo–Mo bond length of 2.532 (1) Å may be somewhat longer than expected for a $\sigma^2\pi^4$ triple bond formulation,[9] but since this is the first example of such a bond which contains μ-phosphido groups, there are no good models with which to compare this complex. A recently described phosphido-bridged Mo_2 quadruple bond was also found to be longer than usually observed.[10] An alternative Mo(II)–Mo(II) single bond formulation would be expected to have a bond length in excess of 3.0 Å.[2]

Consonant with the metal–metal unsaturation, we find that **4** is reactive toward both nucleophiles and electrophiles. Reaction of **4** with 1 equiv of diphenylphosphine gave an air-sensitive complex formulated as **5** based on its spectroscopic data: $^{31}P\{H\}$ NMR ($CDCl_3$) δ 134 (t, J = 6 Hz),, 117 (dd, J = 12, 6 Hz), and 57 (dd, J = 12, 5 Hz, ^1H-coupled, $^1J_{PH}$ = 358 Hz).[4] Reaction with carbon monoxide (1 atm, C_6H_6 solution, 16 h) produced a new species formulated as **6**. The spectroscopic data indicated identical environments for the phosphorus atoms but different ones for the Cp protons as shown in **6**: $^{31}P\{H\}$ NMR (CH_2Cl_2) δ 102 (s); ^1H NMR (C_6D_6) δ 5.40 (s, Cp), 4.50 (s, Cp).[4] Reaction of **4** with excess trifluoroacetic acid gave quantitatively a complex that we formulate as **7**, which featured $^{31}P\{H\}$ NMR ($CDCl_3$) absorptions at δ 155 (d) and 134 (d, J = 43 Hz).[4] We are in the process of confirming this structure by X-ray crystallography.[11] Finally, reaction of **4** with $Fe_2(CO)_9$ in THF at 25 °C for 2 h followed by heating at reflux for 2 h gave a high yield of a green crystalline material **8**,, which analyzed for $[\mathbf{4} + Fe(CO)_4]$: $^{31}P\{H\}$ NMR (CH_2Cl_2, 35 °C) δ 138 (br s); (CH_2Cl_2, −80 °C) δ 194 (br s), 85 (br s).[4] We are currently investigating the structure of this fluxional complex, as well as other aspects of the chemistry of **4** and its congeners.

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Registry No. 1, 38032-29-9; **2**, 12091-64-4; **3**, 90991-31-4; **4**, 90991-32-5; **5**, 90991-33-6; **6**, 90991-34-7; **7**, 90991-35-8; **8**, 15281-98-8; Ph_2PH, 829-85-6; CO, 630-08-0; TFA, 76-05-1; $Fe_2(CO)_9$, 15321-51-4; Mo, 7439-98-7.

Supplementary Material Available: Spectroscopic and analytical data for compounds **3**–**8**, as well as a description of the **3** → **4** reaction, crystallographic details, including tables of positions and equivalent isotropic parameters, and selected distances and angles (9 pages). Ordering information is given on any current masthead page.

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(11) Since submission of this work for publication, we have indeed confirmed the structure of **7** by X-ray crystallography.

Use of Deuterium Labeling To Assess the Roles of Tetramethylammonium Cation, Dimethylformamide, and Water as Proton Donors for Electrogenerated *tert*-Butyl Carbanions. Evidence for the Formation of an Ylide (Trimethylammonium Methylide)

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Recently, in studying[1] the reduction of *tert*-butyl bromide at mercury in dimethylformamide containing tetramethylammonium perchlorate, we became interested in assessing the roles of the solvent, the supporting-electrolyte cation, and water (typically present as an impurity at concentrations ranging from approximately 10 to 50 mM, depending on the procedures used to dry and handle the solvent) as proton donors for the electrolytically generated *tert*-butyl carbanion. From electrolyses involving deuterated reagents, we conclude that the solvent (dimethylformamide) is a poor source of protons for *tert*-butyl carbanions, that water is the dominant proton donor, that the tetramethylammonium cation is the second most important source, and that only a small percentage of the carbanions is protonated by the starting material under the conditions of our experiments.

In a paper by de la Torre and Sease,[2] who summarize earlier work dealing with the elucidation of the roles of proton donors in organic electrochemistry, the reduction of iodobenzene at a mercury cathode in dimethylformamide containing tetraethylammonium bromide and various concentrations of H_2O and D_2O was scrutinized to ascertain the source of protons for electrogenerated phenyl carbanions; these authors found that water is the best proton donor, that the tetraethylammonium cation is a significant source of protons, and that dimethylformamide can serve as a proton donor only if both water and the tetraethylammonium ion are either absent or present at low concentrations. To the best of our knowledge, there have been no previous electrochemical investigations of the role as a proton donor of the tetramethylammonium cation—which, instead of undergoing a Hofmann elimination after deprotonation, would be converted to a nitrogen ylide (trimethylammonium methylide)—nor have there been any reported efforts with deuterated solvent to determine whether dimethylformamide functions as a source of protons for electrogenerated alkyl carbanions.

A normal dc polarogram for *tert*-butyl bromide in dimethylformamide containing 0.1 M tetramethylammonium perchlorate exhibits two waves of nearly identical height with half-wave potentials of −1.23 and −1.46 V;[3] the first wave signals the formation of the *tert*-butyl radical and the second wave is attributable to production of the *tert*-butyl carbanion. Earlier polarographic studies by Fry and Krieger[4] have indicated that *tert*-butyl bromide can undergo stepwise reduction in dimethyl sulfoxide containing various tetraalkylammonium salts. Our electrolysis of *tert*-butyl

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bromide at a mercury pool cathode, under the same conditions as those used to record polarograms, yield isobutane (43%), isobutylene (44%), and 2,2,3,3-tetramethylbutane (9%) as major products at a potential (−1.40 V) corresponding to the first polarographic wave, whereas isobutane (50%) and isobutylene (47%) are the predominant species obtained from electrolyses at a potential (−1.70 V) on the plateau of the second polarographic wave. Product distributions at each potential do not vary for concentrations of water between 5 and 50 mM. In addition, the *apparent* coulometric n value is essentially unity regardless of potential, although evidence to be published elsewhere[1] demonstrates that the *tert*-butyl carbanion is indeed the intermediate produced at a potential (−1.70 V) corresponding to the second polarographic wave; the apparent n value of 1 at the more negative potential is due to the fact that approximately one-half of the alkyl bromide undergoes a non-electron-consuming, base-promoted dehydrohalogenation.

When an electrolysis of 2.5 mM *tert*-butyl bromide was performed at −1.70 V in unlabeled solvent-supporting electrolyte containing 5 mM H_2O and 50 mM D_2O, 42% of the isobutane was determined (by means of mass spectrometry) to be monodeuterated. If we assume a kinetic isotope ratio (k_H/k_D) of 1.25, a figure based on the work of de la Torre and Sease,[2] we estimate that approximately 47% of the *tert*-butyl carbanions generated by electrolysis of the starting material at −1.70 V are protonated by water (at a concentration of 55 mM in the solvent-supporting electrolyte). We know from previous investigations that higher concentrations of water (present as D_2O) protonate even larger percentages of electrogenerated alkyl carbanions; in dimethylformamide containing 0.1 M tetramethylammonium perchlorate and 1 M D_2O, 82% of the decane derived from 1-iododecane[5] and 66% of the octane obtained from 2-iodooctane[6] are deuterated. Our results with *tert*-butyl bromide show clearly that electrogenerated *tert*-butyl carbanions must be protonated by species in the system other than water.

Perdeuterated tetramethylammonium perchlorate ($(CD_3)_4NClO_4$) was prepared from $(CD_3)_4NCl$ by metathesis with silver perchlorate. An electrolysis of 2.5 mM *tert*-butyl bromide at −1.70 V in dimethylformamide containing 0.1 M $(CD_3)_4NClO_4$ and approximately 15 mM H_2O gave the expected yield of isobutane, 34% of which was found to be monodeuterated. One can question whether deuterons from $(CD_3)_4N^+$ enter the H_2O pool via a sequence of protonation–deprotonation (scrambling) reactions, thereby becoming available as HDO or D_2O to form monodeuterated isobutane from electrogenerated *tert*-butyl carbanions. We have tested this possibility in a separate chemical experiment with a solution initially containing 30 mM $(CD_3)_4NClO_4$, 15 mM OH^- in the form of $(CH_3)_4NOH{\cdot}5H_2O$, and 15 mM H_2O in dimethylformamide. By the time $(CH_3)_4NOH{\cdot}5H_2O$ dissolved—approximately 60 min (comparable to the duration of an exhaustive electrolysis of *tert*-butyl bromide)—NMR spectra recorded with the aid of a Nicolet NT-360 instrument revealed that the extent of deuterium scrambling was only 24% of the theoretical maximum. When all the preceding results are considered together, we conclude that the transfer of protons (deuterons) from tetramethylammonium cations to *tert*-butyl carbanions takes place *directly*

$$(CH_3)_3C^- + (CD_3)_4N^+ \rightarrow (CH_3)_3CD + (CD_3)_3N^+CD_2^-$$

as well as *indirectly* via proton (deuteron) scrambling:

$$(CH_3)_3C^- + H_2O \rightarrow (CH_3)_3CH + OH^-$$

$$OH^- + (CD_3)_4N^+ \rightleftharpoons HDO + (CD_3)_3N^+CD_2^- \rightleftharpoons OD^- + (CD_3)_3N^+CD_2H$$

$$OD^- + H_2O \rightleftharpoons HDO + OH^-$$

$$(CH_3)_3C^- + HDO \rightarrow (CH_3)_3CD + OH^-$$

As a consequence of proton (deuteron) scrambling, the experimentally measured yields of monodeuterated isobutane formed in the presence of various sources of deuterons do not indicate the relative rates of *direct* proton (deuteron) donation to the *tert*-butyl carbanion by these species.

Another electrolysis was done at −1.70 V with a 2.5 mM solution of $(CD_3)_3CBr$ in unlabeled dimethylformamide containing 0.1 M $(CH_3)_4NClO_4$ and 8 mM H_2O; 5% of the resulting isobutane[7] was found to be $(CD_3)_3CD$, which could originate via attack of $(CD_3)_3C^-$ on unreduced $(CD_3)_3CBr$. Perdeuterated dimethylformamide ($DCON(CD_3)_2$) was used as solvent for the electrolysis of 2.5 mM *tert*-butyl bromide at −1.70 V in the presence of 0.1 M $(CH_3)_4NClO_4$ and 14 mM H_2O; no more than 1% of the resulting isobutane was monodeuterated.

We are intrigued by the likelihood that an ylide (trimethylammonium methylide) is formed by deprotonation of the supporting-electrolyte cation and by the prospect that electrolyses of alkyl halides (at potentials corresponding to the production of carbanion intermediates) in dimethylformamide containing tetramethylammonium perchlorate could afford a way to generate the ylide for other chemical purposes.

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Bis(nitroxyl) Radical Adducts of Rhodium(II) and Molybdenum(II) Carboxylate Dimers: Magnetic Exchange Interactions Propagated by Metal–Metal Bonds

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Interactions between paramagnetic centers connected by a continuous bonding framework provide models for thermal and photochemical processes[1] and probes into the transition metal to ligand orbital interface.[2] The magnitude of such a magnetic exchange interaction, gauged by the exchange parameter J, contains sensitive information about the electronic structure of the atomic or molecular bridging moiety connecting the two paramagnets. The effectiveness of an extended bridging group to propagate an exchange interaction offers insight into possible pathways of electron transfer in solution redox reactions (whether of the inner- or outer-sphere type),[3] in biological electron-transport chains,[4] and in mixed-valence compounds.[5] The existence of a

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