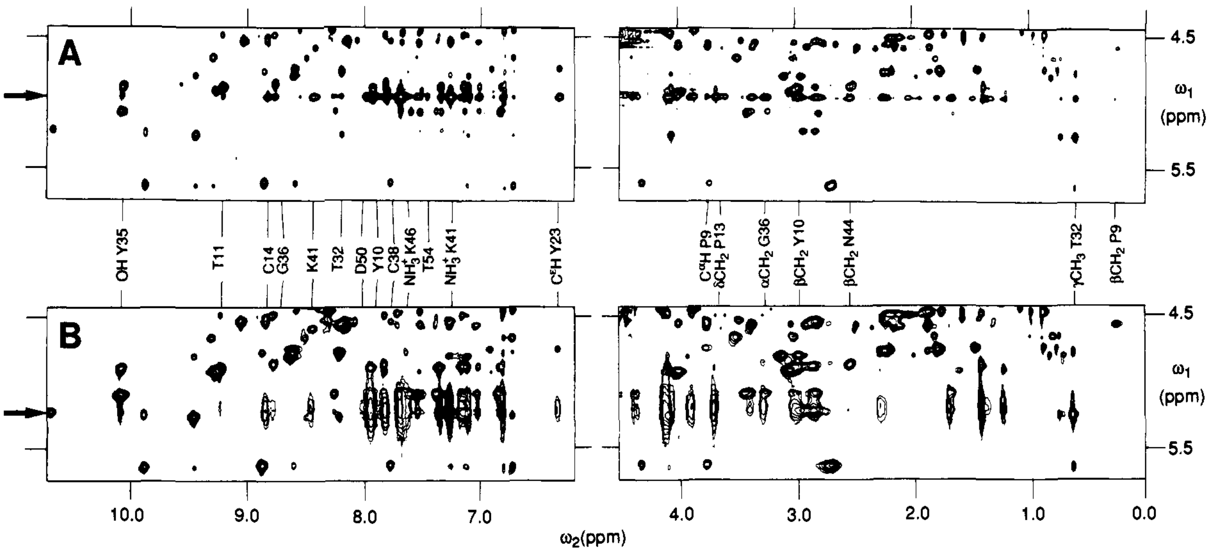

Figure 1. Spectral regions (ω_1 = 4.4–5.8 ppm, ω_2 = 0.0–4.5 and 6.2–10.2 ppm) of two homonuclear 2D [^{1}H,^{1}H]-NOESY spectra recorded at 4 °C with a 20 mM solution of BPTI in 90% H_2O/10% D_2O, pH 3.5, with and without addition of the shift reagent $CoCl_2$, using the experiment described in ref 3 (^{1}H frequency = 600 MHz, t_{1max} = 60 ms, t_{2max} = 150 ms, sweep width in ω_1 and ω_2 6944 Hz, total measuring time 12 h). The spectra were base-line-corrected in both dimensions, using polynominals. The arrows on the left indicate the ω_1 frequency of the water signal. The contour levels were plotted on an exponentially increasing scale, where each level is $2^{1/2}$ times higher than the preceding one. (A) Without $CoCl_2$, mixing time = 112 ms. (B) With 30 mM $CoCl_2$, mixing time = 90 ms. Lower contour levels are plotted than in A. In the center the cross peaks with the water resonance are identified with the one-letter amino acid symbol, the sequence position, and except for the backbone amide protons, the proton positions in the amino acid residues.[3] Some of the signals seen in A are below the lowest plot level in B because of the line broadening.

1 presents unambiguous evidence that the apparent ^{1}H chemical shift equivalence between bulk water and interior water molecules is related to the chemical exchange reaction described by eq 2. For the reaction rate a lower limit of $k_m > 50$ s^{-1} was established from the following considerations. Although the observations in Figure 1 would be compatible with the assumption that the resonance lines of the bulk water and the interior water are coalesced or that the resonances of the interior waters are separated from that of the bulk water but exchange-broadened beyond detection (this would be the case for $k_m > 10^3$ s^{-1}), the above, more conservative estimate for k_m is obtained assuming that the resonance lines of the interior waters are resolved, but lie within 0.4 ppm of the bulk water resonance and thus are concealed by the water suppression technique used.[3] In this situation, an exchange rate of $k_m > 50$ s^{-1} would be sufficient to quench the cross peaks with the protein signals, since the magnetization would be rapidly transferred from the interior waters to the bulk water during the NOESY mixing time. The efficient relay of magnetization from the bulk water to the hydration sites would then also account for the cross peaks observed between bulk water and protein protons. Combined with the previously estimated lower limit,[3] we then have that, at 4 °C, 20 ms > τ_m > 0.3 ns. The available evidence[3-6] supports that these measurements with BPTI present a realistic guideline also for interior hydration of other globular proteins.

Because the experiment of Figure 1 provides direct information only on the upper limit for τ_m of the *protons* of interior water molecules, we performed similar experiments also with ^{17}O NMR, using 10% ^{17}O-enriched water as the solvent and $CoCl_2$ and $DyCl_3$ as shift reagents. In contrast to similar experiments with slowly exchanging water molecules bound to diamagnetic metal ions,[11] no separate ^{17}O line of BPTI-bound water could be observed. This result would be consistent with the view that the limiting value of τ_m < 20 ms for the lifetime of the interior hydration water in BPTI is valid not only for the water protons but also for the entire water molecules. It is not clear, however, that this conclusion is warranted, since there is the alternative explanation that the ^{17}O signal of protein-bound water could be broadened beyond detection due to the efficient nuclear quadrupole relaxation in the slow motional regime, which has not been properly excluded. In this context it should be recalled that, in earlier experiments with BPTI using gel filtration techniques with ^{18}O-enriched water, the ^{18}O exchange was complete within the deadtime of the experiment, which was 10 s.[12]

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Spectroelectrochemical Study of the C_{60} and C_{70} Fullerenes and Their Mono-, Di-, Tri-, and Tetraanions

Dominique Dubois and Karl M. Kadish*

Department of Chemistry, University of Houston
Houston, Texas 77204-5641

Scott Flanagan, R. E. Haufler, L. P. F. Chibante, and
Lon J. Wilson*

Department of Chemistry and the Laboratory for
Biochemical and Genetic Engineering
William Marsh Rice University
P.O. Box 1892, Houston, Texas 77251-1892

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The recent synthesis of macroscopic amounts of the third allotropic form of carbon, C_{60} or buckminsterfullerene,[1] has prompted a flurry of research into its structure, properties, and reactivity.[2-8] Some of us reported the first electrochemical study of C_{60} which characterized the C_{60}^- and C_{60}^{2-} buckide anions in CH_2Cl_2 by cyclic voltammetry.[9] Subsequently, an electrochemical

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(1) Krätschmer, W.; Fostiropoulos, K.; Huffman, D. R. *Chem. Phys. Lett.* **1990**, *170*, 167. Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.

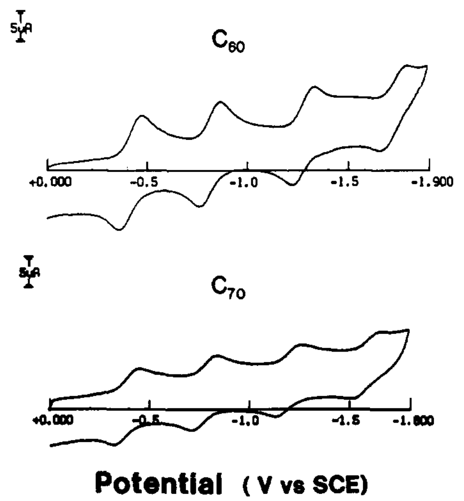

Figure 1. Cyclic voltammograms at a platinum electrode in CH_2Cl_2, 0.05 M $[(n\text{-}Bu)_4N](BF_4)$, for C_{60} at 10 V/s and C_{70} at 20 V/s.

study of C_{60} and its related fullerene, C_{70}, documented a third reduction process.[6] This communication extends our original work through a spectroelectrochemical characterization of the C_{60}^{n-} and C_{70}^{n-} (n = 1, 2) radical anions and reports a fourth one-electron reduction for both C_{60} and C_{70}.

Figure 1 presents cyclic voltammograms of C_{60} and C_{70} in CH_2Cl_2. C_{60} exhibits reductions at a scan rate of 20 V/s at $E_{1/2}$ = −0.44, −0.82, −1.25, and −1.72 V vs SCE. All four processes are reversible in a conventional electrochemical cell,[10] but only the first two appear reversible at slow scan rates (0.1 V/s) or in the thin-layer cell used for spectroelectrochemistry.[11] Controlled-potential coulometry establishes the first two reductions as fully reversible one-electron transfers. The system could be reduced and reoxidized several times without significant loss of reversibility (as judged by the constant charge transferred and the well-defined cyclic voltammograms obtained for electrolyzed solutions). Reduction of C_{60} to each C_{60}^{n-} level (n = 1, 2, 3, 4) has been verified to involve a one-electron transfer by analysis of the voltammetric data at 20 V/s. Bulk electrolysis to produce C_{60}^{3-} gives complicated current–time curves and is not reversible.

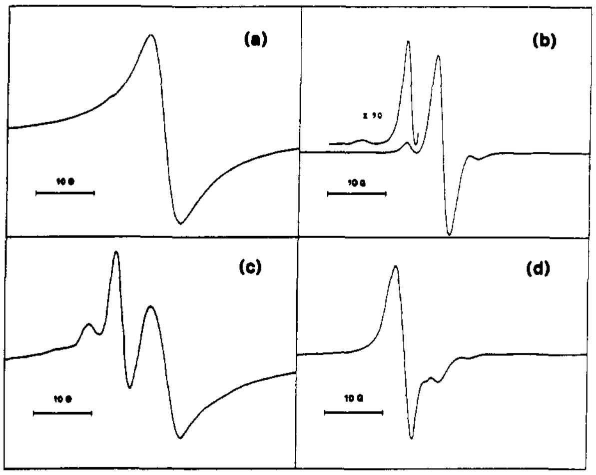

Figure 2. EPR spectrum at 120 K of a frozen CH_2Cl_2 glass, containing electrochemically generated (a) C_{60}^-, (b) C_{60}^{2-}, (c) C_{70}^-, and (d) C_{70}^{2-}. All spectra are centered at 3350 G.

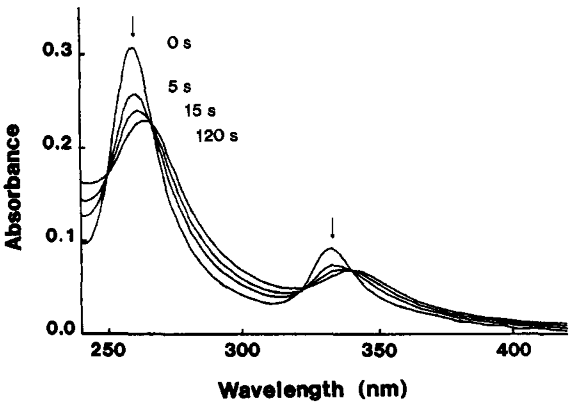

Figure 3. Time-dependent electronic absorption spectrum for the C_{60} reduction to C_{60}^- in CH_2Cl_2, 0.05 M $[(n\text{-}Bu)_4](BF_4)$, by thin-layer controlled-potential electrolysis at −0.60 V vs SCE.

As shown in Figure 1, C_{70} also displays four consecutive reductions at $E_{1/2}$ = −0.41, −0.80, −1.20, and −1.58 V vs SCE. Each reduction is reversible at a scan rate of 20 V/s in a conventional cell, but only the first two display full reversibility in the thin-layer cell. Analysis of the voltammogram in Figure 1 establishes all four reductions to be one-electron transfers. The third reduction produces a very reactive species, presumably C_{70}^{3-}; thus coulometry could not be used to verify this level of reduction. The bulk electrolysis of C_{70} to C_{70}^{3-} is not fully reversible, but the process exhibits some reversibility as determined by the shape of the resulting current–time curves and by the voltammetric data of the electrolyzed solution. The third reduction of C_{70} is reversible by cyclic voltammetry at 0.1 V/s, but this is not the case for C_{60}, thus indicating that C_{70}^{3-} is less reactive in CH_2Cl_2 than C_{60}^{3-}.

Controlled-potential electrolysis at potentials ca. 0.2 V more negative than each $E_{1/2}$ establishes that 1.0 ± 0.1 electrons are transferred for formation of C_{60}^- and C_{70}^- and 2.0 ± 0.1 electrons for C_{60}^{2-}. Resetting the potential to 0.00 V quantitatively regenerates C_{60} and C_{70}, as evidenced by recovery of the initial solution color, the original UV–vis spectrum, and/or the original cyclic voltammogram.

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(10) Cyclic voltammograms were recorded by using a conventional three-electrode configuration. The working electrode was a platinum button and the counter electrode a platinum wire. A saturated calomel electrode (SCE) was used as the reference electrode and was separated from the bulk of the solution by a fritted-glass bridge. A BAS 100 electroanalyzer interfaced with a Houston Instruments HIPLOT DMP-40 apparatus was used to record current–voltage curves. Bulk controlled-potential electrolysis was performed in a Vacuum Atmosphere glovebox with the use of an EG&G Model 173 potentiostat. An EG&G Model 179 X-Y digital coulometer was used to record the current–time curves and the resulting total charge transferred during controlled-potential electrolysis.

(11) Thin-layer spectroelectrochemical measurements were performed with an EG&G Model 173 potentiostat coupled to a Princeton Instruments Model ST-1000 optical multichannel analyzer. A deuterium or xenon lamp was utilized as the light source. The optically transparent platinum thin-layer electrode (OTTLE) was constructed from either regular or quartz glass according to our design (ref 12). EPR spectra were recorded on a Brüker Model 100D spectrometer.

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EPR spectra of frozen solutions containing electrochemically generated C_{60}^-, C_{60}^{2-}, C_{70}^-, and C_{70}^{2-} are displayed in Figure 2.[13] The 120 K EPR spectrum of C_{60}^- shows only slight anisotropy with $g = 2.001$ and a peak to peak separation of 5.5 G. In contrast, the low-temperature spectrum of C_{70}^- is quite anisotropic and three g values are readily discerned at $g = 2.007$, 2.003, and ~2.000. The greater anisotropy for C_{70}^- seems reasonable in view of the fact that the symmetry of C_{70} is only D_{5h} compared to I_h for C_{60}. The C_{70}^{2-} resonance also displays greater anisotropy than the C_{60}^{2-} resonance. The spectrum of C_{60}^{2-} is a "quintet" centered at $g = 2.003$. The first set of satellites are 6.3 G (left) and 6.2 G (right) away from the main resonance. A second pair of satellites, of much lower intensity, lies further out at 13.9 G (left) and 14.0 G (right) from the center signal. Assuming that C_{60}^{2-} is an $S = 1$ diradical, its EPR spectrum shows more complexity than the triplet that should arise from simple dipolar coupling. This complexity probably arises from exchange coupling, and spectral simulation studies will be needed for a full interpretation of the spectrum.

C_{60} exhibits two prominent UV-visible bands at 257 and 330 nm in CH_2Cl_2 (0.05 M $[(n\text{-Bu})_4N](BF_4)$) similar to the spectra reported in hexane.[3,4] Both major bands of C_{60} are replaced by bands of somewhat lower intensity at 262 and 339 nm after electrolysis is completed to produce C_{60}^-. Figure 3 displays the time-dependent spectrum obtained between 240 and 420 nm during electrolysis of C_{60} to produce C_{60}^-; the clean isosbestic points indicate the presence of only two spectrally detectable species in solution. A second reduction to C_{60}^{2-} gives a spectrum with broad bands at 263 and 340 nm. The conversion of C_{60}^- to C_{60}^{2-} also displays well-defined isosbestic points. The original C_{60} spectrum could be regenerated by reoxidation of C_{60}^- or C_{60}^{2-} at 0.00 V, thus demonstrating a high degree of reversibility for both processes. Similar behavior is observed upon reduction of C_{70}.[14]

In conclusion, this work reports the UV-vis and EPR spectra of the C_{60}^{n-} and C_{70}^{n-} ($n = 1, 2$) anions by spectroelectrochemical techniques. The EPR spectra suggest that the anions exist as radicals with $S = {}^1/_2$ ($n = 1$) and $S = 1$ ($n = 2$) ground states. In addition, a third reduction of C_{60}^{3-} and C_{70}^{3-} has been verified and a fourth reduction to C_{60}^{4-} and C_{70}^{4-} is reported for the first time.

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[13] Samples for the EPR experiments were immediately collected from the freshly electrolyzed solutions, transferred into EPR tubes in the glovebox, promptly taken out of the box, and frozen in liquid nitrogen (and subsequently kept as such).

[14] UV-visible bands in CH_2Cl_2: C_{70} (333, 362, 381, and 466 nm); C_{70}^- (340, 386, and 483 nm; broadened). The C_{70}^{2-} spectrum is almost featureless except for a few ill-defined shoulders and two weak bands (609 and ca. 636 nm).

Agreement of Proton Transfer Cross Reaction Rates between Transition Metals with Those Predicted by Marcus Theory

S. Sôley Kristjánsdóttir and Jack R. Norton*

Department of Chemistry, Colorado State University
Fort Collins, Colorado 80523

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Marcus noted in 1968[1] that a cross relation like the one he had derived for electron transfer should also apply to proton transfer.[2] If the intrinsic barrier $\Delta G_0^\ddagger$ for proton transfer from A to B (eq 1) is the average[3] of $\Delta G_{AA}^\ddagger$ and $\Delta G_{BB}^\ddagger$, the barriers to proton self-exchange for A and B, respectively, the basic Marcus relation[4] gives eq 2 for $\Delta G_{AB}^\ddagger$.[5-7] Restatement of eq 2 in terms of the corresponding rate and equilibrium constants gives eq 3, a cross relation like that familiar for electron transfer.

$$\text{A–H} + \text{B}^- \underset{k_{BA}}{\overset{k_{AB}}{\rightleftharpoons}} \text{A}^- + \text{B–H} \qquad K_{AB} = k_{AB}/k_{BA} \tag{1}$$

$$\Delta G_{AB}^\ddagger = {}^1\!/_2[\Delta G_{AA}^\ddagger + \Delta G_{BB}^\ddagger + \Delta G^\circ] \tag{2}$$

$$k_{AB} = \sqrt{k_{AA}k_{BB}K_{AB}} \tag{3}$$

Rate data are available for many proton transfer reactions where only one partner has a large intrinsic barrier: for example, the deprotonation of carbon acids by oxygen and nitrogen bases[5] and the deprotonation of transition-metal hydrides by nitrogen bases.[8] However, the validity of eqs 2 and 3 for systems *where both $\Delta G_{AA}^\ddagger$ and $\Delta G_{BB}^\ddagger$ are significant* has not been demonstrated experimentally. The slow H^+ exchange between 9-alkylfluorene and (9-alkylfluorenyl)lithium in ether does not obey eqs 2 and 3, perhaps because of the degree to which the (9-alkylfluorenyl)lithium is ion paired.[9] However, because carbonylmetalate anions do not form contact ion pairs in CH_3CN,[10] and because the conjugate transition-metal acids do not hydrogen bond to bases,[11] the apparent rate constants measured for the proton-transfer reactions of these acids should be those of the H^+ transfer steps themselves, and the rate constants for their cross reactions

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[1] Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891.

[2] Later theoretical work has successfully treated H^+ transfer with a weak interaction model: (a) Dogonadze, R. R.; Kuznetsov, A. M.; Levich, G. *Electrochim. Acta* **1968**, *13*, 1025. (b) German, E. D.; Kuznetsov, A. M.; Dogonadze, R. R. *J. Chem. Soc., Faraday Trans. 2* **1980**, 1128. (c) Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1988**, *110*, 2418. (d) Siebrand, W.; Wildman, T. A.; Zgierski, M. Z. *J. Am. Chem. Soc.* **1984**, *106*, 4083.

[3] Such an assumption is plausible during *electron* transfer because "the force field from one reactant does not influence the other",[4a] but it is less clear a priori that is true during *proton* transfer (which obliges the reactants to come into relatively close contact). Marcus remarked while discussing proton transfers in 1968 that "additivity might be expected to hold best if neither [intrinsic barrier] is near zero"[5a] and later used a simple BEBO model to show that it is not seriously in error even when one intrinsic barrier is substantially larger than the other.[5c]

[4] (a) Marcus, R. A. *J. Chem. Phys.* **1968**, *43*, 679. (b) Newton, T. W. *J. Chem. Educ.* **1968**, *45*, 571.

[5] Detailed discussions of the application of Marcus theory to proton-transfer reactions can be found in the following: (a) Cohen, A. O.; Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 4249. (b) Marcus, R. A. *J. Am. Chem. Soc.* **1969**, *91*, 7225. (c) Marcus, R. A. *Faraday Symp. Chem. Soc.* **1975**, *10*, 60. (d) Kresge, A. J. *Chem. Soc. Rev.* **1973**, *2*, 475. (e) Bell, R. P. *The Proton in Chemistry*; Cornell University Press: Ithaca, NY, 1973. (f) Albery, W. J. *Annu. Rev. Phys. Chem.* **1980**, *31*, 227. (g) Stewart, R. *The Proton: Applications to Organic Chemistry*; Academic: New York, 1985.

[6] Substitution of $\Delta G_0^\ddagger = (1/2)[\Delta G_{AA}^\ddagger + \Delta G_{BB}^\ddagger]$ into the basic Marcus relation[4] $\Delta G^\ddagger = (1 + \Delta G^\circ/4\Delta G_0^\ddagger)^2\Delta G_0^\ddagger$ and acceptance of the restriction that $\Delta G^\circ < 4\Delta G_0^\ddagger$ lead to eq 2. For slow proton transfers with large intrinsic barriers and relatively modest thermodynamic driving forces, the quadratic term can, as with methyl transfers,[7] be neglected. Marcus originally noted[1] that the application of cross relations like eqs 2 and 3 to proton transfers was probably limited to $|\Delta G^\circ/4\Delta G_0^\ddagger| < 1$.

[7] Lewis, E. S. *J. Phys. Chem.* **1986**, *90*, 3756. (Lewis does state that proton transfers are a case where a contribution from the quadratic term is possible.)

[8] (a) Edidin, R. T.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3945. (b) Weberg, R. T.; Norton, J. R. *J. Am. Chem. Soc.* **1990**, *112*, 1105.

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[10] No contact ion pair formation between any organometallic anion and Na^+, K^+, or PPN^+ has ever been observed in CH_3CN.[8a,b,10a-g] There is weak interaction between Tl^+ and $[Co(CO)_4]^-$ in CH_3CN.[10b] (a) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257. (b) Schramm, C.; Zink, J. I. *J. Am. Chem. Soc.* **1979**, *101*, 4554. (c) Bockman, T. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 4669. (d) Edgell, W. F.; Barbetta, A. *J. Am. Chem. Soc.* **1974**, *96*, 415. (e) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255. (f) Jordan, R. F.; Norton, J. R. *ACS Symp. Ser.* **1982**, *198*, 403. (g) Darensbourg, M. Y.; Jimenez, P.; Sacket, J. R.; Hanckel, J. M.; Kump, R. L. *J. Am. Chem. Soc.* **1982**, *104*, 1521. For a review, see: Kristjánsdóttir, S. S.; Norton, J. R. Acidity of Hydrido Transition Metal Complexes in Solution. In *Transition Metal Hydrides: Recent Advances in Theory and Experiment*; Dedieu, A., Ed.; VCH: New York, in press.

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