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# Notes

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## Photochemistry of a Square-Planar Cobalt(III) Complex

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and Kirk S. Schanze*

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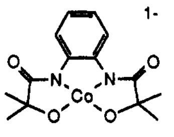
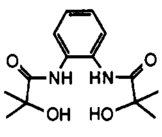
The synthesis, structure, and catalytic properties of the square-planar Co(III) complex **1** have recently been reported.[1-3]



**1**



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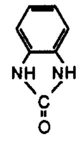
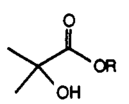
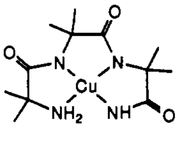


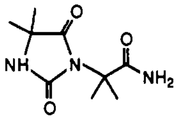
**3**



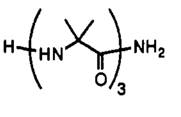
**4a** (R = H)
**4b** (R = OMe)
**4c** (R = O-iPr)



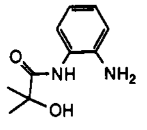
**5**



**6**



**7**



**8**

We recently initiated a photochemical investigation to assess the possible use of **1** as a photooxidant. These studies indicate that photolysis of **1** in the presence of primary and secondary alcohols does not effect alcohol oxidation;[4] however, photoinduced decomposition of **1** is observed. The present communication describes a study concerning the photochemical decomposition of **1**. Interestingly, product and quantum yield studies suggest that the photoreaction occurs via a novel mechanism that is very similar to one operating in the photodecomposition of Cu(III)–peptide complexes.[5-7] The remarkable parallels in the photochemistry of the Co(III) and Cu(III) systems are attributed to the fact that in each case LMCT excitation leads to intraligand carbon–carbon bond cleavage and formation of an intracomplex isocyanate intermediate.

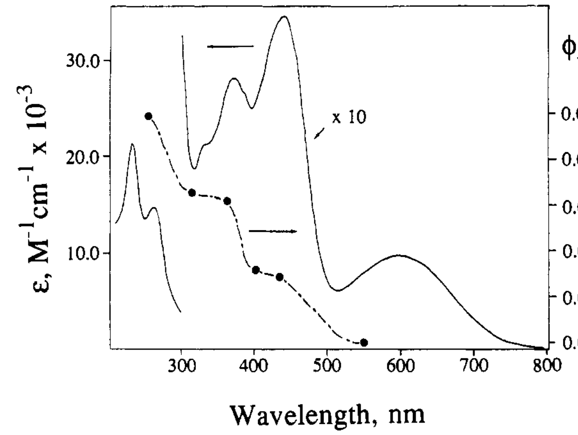


**Figure 1.** (—) UV–visible absorption spectrum of Na–**1** in $H_2O$ (scale given at left). Note that absorption from 310 to 800 nm is increased by a factor of 10. (---•) Wavelength dependence of quantum yield for disappearance of Na–**1** in $H_2O$ (scale given at right). Measurements were carried out at 254, 313, 366, 404, 436, and 546 nm (data indicated by dark circles). Dashed line represents the extrapolation of data.

### Experimental Section

Ligand **2** was prepared by the literature method[8] and recrystallized from acetone/water.[9] The metal complex salts Na–**1** and $PPh_4$–**1** were prepared by literature methods[1] and purified by recrystallization from acetone and water, respectively.[10]

Preparative-scale irradiations were carried out by using a 450-W medium-pressure Hg lamp that was filtered through a $CuSO_4$ solution to isolate the 366-nm Hg emission. The nonvolatile organic reaction products **2** and **3** were isolated by semipreparative HPLC using a Du Pont $C_{18}$ reversed phase column and eluting with 80% MeOH/$H_2O$. The volatile products **4** and acetone were detected and analyzed by capillary GC and GC-MS.

Quantum yields for disappearance of Na–**1** were determined by monitoring the decrease in absorbance of the complex at various irradiation times up to 15% conversion. Quantum yields for formation of **2** and **3** were determined by HPLC analysis of solutions irradiated to 15% conversion. Each quantum yield determination was repeated three times, and the standard deviations were generally <10% of the reported average value. The irradiation source consisted of a 75-W high-pressure Hg lamp contained in an elliptical reflector housing. The optical output was passed through an IR filter and a monochromator and then focused into a 1-cm cuvette containing the photolysis solution and a stir bar. Actinometry was carried out by using Aberchrome 540 or potassium ferrioxalate actinometers.[11,12]

### Results

The UV–visible absorption spectrum of Na–**1** in $H_2O$ is displayed in Figure 1. Absorption maxima and extinction coefficients [λ, nm (ε, M$^{-1}$ cm$^{-1}$)]: 600 (890), 434 (3240), 370 (2920), 262 (15300), 231 (21800). The relatively weak, low-energy absorption band at 600 nm is assigned to a ligand field (LF) transition,[13-15]

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(1) Collins, T. J.; Richmond, T. G.; Santarsiero, B. D.; Treco, B. G. R. T. *J. Am. Chem. Soc.* **1986**, *108*, 2088.

(2) Collins, T. J.; Ozaki, S.; Richmond, T. G. *J. Chem. Soc., Chem. Commun.* **1987**, 803.

(3) Brewer, J. C.; Collins, T. J.; Smith, M. R.; Santarsiero, B. D. *J. Am. Chem. Soc.* **1988**, *110*, 423.

(4) Complex **1** ($c$ = $10^{-4}$ M) was photolyzed with benzyl alcohol or diphenylmethanol ($c$ = 1.0 M). No oxidation products were detected by HPLC analysis. The expected oxidation product for benzyl alcohol is benzaldehyde or benzoic acid, and that for diphenylmethanol is benzophenone. The limit for detection of these products is ≈5 × $10^{-6}$ M (yield ≤5% based on disappearance of **1**).

(5) Kirksey, S. T., Jr.; Neubecker, T. A.; Margerum, D. W. *J. Am. Chem. Soc.* **1979**, *101*, 1631.

(6) Hamburg, A. W.; Margerum, D. W. *Inorg. Chem.* **1983**, *22*, 3884.

(7) Hinton, J. P.; Margerum, D. W. *Inorg. Chem.* **1986**, *25*, 3248.

(8) Anson, F. C.; Collins, T. J.; Richmond, T. G.; Santarsiero, B. D.; Toth, J. E.; Treco, B. G. R. T. *J. Am. Chem. Soc.* **1987**, *109*, 2974.

(9) Spectral data for **2**: $^1$H NMR, $D_2O$/NaOD (ppm) 1.39 (s, 12 H), 7.33 (m, 4 H); $^{13}$C NMR, $D_2O$/NaOD (ppm) 29.5, 76.5, 129.1, 130.7, 133.1, 181.8.

(10) Spectral data for Na–**1**: $^1$H NMR, $D_2O$ (ppm) −23.3 (s, 2 H), 1.7 (s, 2 H), 8.4 (s, 12 H). Anal. Calcd for Na-**1**·$(CH_3)_2CO$: C, 49.04; H, 5.28; N, 6.73. Found: C, 47.37; H, 5.08; N, 6.40.

(11) Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkin Trans. 1* **1981**, 341.

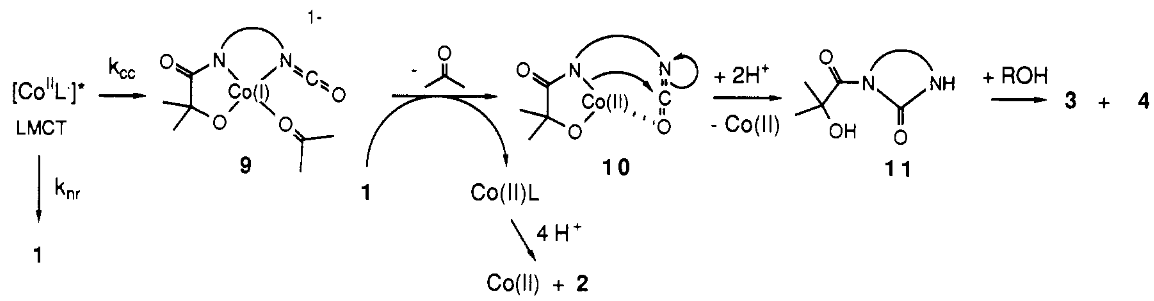
(12) Wegner, E. E.; Adamson, A. W. *J. Am. Chem. Soc.* **1966**, *88*, 394.

(13) Urbach, F. L. In *Coordination Chemistry of Macrocyclic Compounds*; Melson, G. A., Ed.; Plenum: New York, 1979; Chapter 5.

(14) Bosnich, B.; Poon, C. K.; Tobe, M. L. *Inorg. Chem.* **1965**, *4*, 1102.

(15) Sadasivan, N.; Kernohan, J. A.; Endicott, J. F. *Inorg. Chem.* **1967**, *6*, 770.

**Scheme I**



and the two moderately intense bands that occur in the near-UV–visible region are assigned to ligand-to-metal charge-transfer (LMCT) absorptions.[16] The strong bands in the UV region are attributed to a combination of intraligand and LMCT transitions.

Product analysis indicates that irradiation of **1** in $H_2O$, MeOH, and *i*-PrOH leads to the following photochemical reaction:

$$\text{Na-}\mathbf{1} \xrightarrow{h\nu} \text{Co(II)} + \mathbf{2} + \mathbf{3} + \mathbf{4} + \text{acetone} \qquad (1)$$

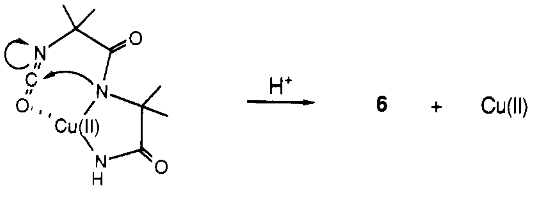
Co(II) was analyzed by adding KSCN to an irradiated solution of **1** in $H_2O$ and monitoring the absorption of $Co(SCN)_4^{2-}$ at 625 nm.[17] Quantitation of the $Co(SCN)_4^{2-}$ absorption band shows that Co(II) is formed in 1:1 stoichiometry relative to disappearance of **1**. Products **2** and **3** were isolated by semipreparative HPLC and identified by using spectroscopic techniques and by comparison with authentic samples.[18] Production of acetone was confirmed by GC analysis of solutions of Na–**1** before and after irradiation. Ester **4b** was identified by GC and GC-MS analysis of a solution of **1** following irradiation in MeOH solution.

Quantum yields for disappearance of Na–**1** ($\Phi^1_-$) were determined in $H_2O$ as a function of wavelength; the data are plotted in Figure 1 to allow comparison with the absorption spectrum of the metal complex. Quantum yields for disappearance of Na–**1** in $H_2O$, MeOH, and *i*-PrOH were determined in air-saturated and Ar-degassed solutions for irradiation at 366 nm. The quantum yields in alcohol solutions were slightly lower compared to those in $H_2O$ ($\Phi^1_-[H_2O] = 0.031$, $\Phi^1_-[\text{MeOH}] = 0.009$, and $\Phi^1_-[i\text{-PrOH}] = 0.002$). In each solvent, $\Phi^1_-$ was the same for air-saturated and degassed solutions.

Quantum yields for formation of **2** and **3** by irradiation of **1** in $H_2O$ at 366 nm were determined by HPLC analysis ($\Phi^2$ and $\Phi^3$, respectively). Uracil was added after irradiation as an internal standard, and the yields were determined relative to bleaching of the UV–visible absorption of **1**. The yields were $\Phi^2 = 0.015$ and $\Phi^3 = 0.014$ in air-saturated and degassed solutions. It is important to note that products **2** and **3** are produced in 1:1 stoichiometry and each is formed in 50% yield relative to disappearance of **1**.

## Discussion

Several important experimental results must be addressed by a mechanism for the photochemical decomposition reaction of **1**. First, photochemistry is only observed as a result of photolysis of the LMCT absorption bands. Second, the observed organic products **2**–**4** and acetone must be explained. Third, the quantum efficiency results indicate that the stoichiometry for formation of **2** and **3** is 50%, each based on loss of **1**. It is important to note that these experimental results are very similar to those observed in a study of the photochemistry of some Cu(III)–peptide complexes.[5-7] Most relevant to the present study is the reaction of the Cu(III) complex **5**, which under LMCT photolysis decomposes to give Cu(II), hydantoin **6**, peptide **7**, and various other decomposition products.[6,7] Importantly, quantum efficiency studies reveal that the yield of **7** is invariably 50% based on loss of starting complex **5**.[6,7] These experimental results led the authors to suggest a mechanism with the following important features.[7] (1) The reaction is initiated by LMCT photoexcitation. (2) Formation of **6** involves loss of two electrons from the complexed peptide ligand: one electron is transferred to the complexed Cu(III) in the process of LMCT excitation, and the second is transferred in a thermal bimolecular reaction to a second Cu(III)–peptide complex. The secondary thermal reaction leads to formation of **7** and Cu(II) and accounts for the 50% yield of **7**. (3) The mechanism for the reaction that results in formation of **6** is suggested to involve intramolecular nucleophilic attack on an isocyanate functional group by a coordinated deprotonated amide nitrogen atom (eq 2). Several parallels exist between the photochemical reactions of Co(III) complex **1** and Cu(III)–peptide complex **5**. First, in each system the reaction is initiated by LMCT excitation. Second, free ligand **2** and free peptide **7** are each formed in 50% yield based upon loss of starting complexes **1** and **5**, respectively. Finally, products **3** and **6** each result from an intramolecular cyclization reaction in which a coordinated amide nitrogen acts as a nucleophile.



(2)

With these considerations in mind, a possible mechanism for the photodecomposition reaction of **1** is outlined in Scheme I. The initial photoevent involves formation of a LMCT excited state via photoinduced transfer of an electron from a ligand-based ($\sigma$ or $\pi$) orbital into the metal center. The LMCT assignment is supported by the observation that **1** is stable to irradiation into the LF band and by the correlation of the wavelength dependence of the quantum yield with the position of the LMCT absorption bands (Figure 1). A similar wavelength dependence is observed in the Cu(III)–peptide system and more generally for LMCT photochemistry in other transition-metal complex systems.[6,7,19-21] The LMCT state subsequently either returns to the ground state via nonradiative decay or relaxes via carbon–carbon bond cleavage within the ligand and transfer of an additional electron to the metal center to produce **9**, which contains Co(I), coordinated acetone, and an isocyanate functional group.[22] Note that the bond that undergoes fragmentation is comparatively weak ($E_{C-C} \leq 75$ kcal/mol).[23] Furthermore, ligand oxidation by LMCT excitation very likely decreases the bond strength further: recent studies show that C–C bond strengths in organic radical cations are substantially lower than in the corresponding parent molecules.[24,25]

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(16) Endicott, J. F. In *Concepts of Inorganic Photochemistry*; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley: New York, 1975; Chapter 3.

(17) Kitson, R. E. *Anal. Chem.* **1950**, *22*, 664.

(18) Spectral data for product **3**: $^1$H NMR (ppm) 2.92 (s, 2 H), 7.0 (m, 4 H); $^{13}$C NMR (ppm) 110.2, 122.3, 136; IR (cm$^{-1}$) 1197, 1272, 1362, 1408, 1486, 1630, 1757, 2800–3200. Mass spectrum: M$^+$, *m/e* 134.

(19) Balzani, V.; Carassiti, V. *Photochemistry of Coordination Compounds*; Academic Press: New York, 1970.

(20) *Concepts of Inorganic Photochemistry*; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley: New York, 1975.

(21) Mok, C. Y.; Hoon, T. G. *Inorg. Chim. Acta* **1982**, *62*, 231.

(22) Species **9** could equivalently be represented by the structure Co$^{II}$L$^{\bullet}$, in which an acetone ketyl anion radical is coordinated to Co(II).

(23) Lowry, T. H.; Richardson, K. H. *Mechanism and Theory in Organic Chemistry*; Harper and Row: New York, 1987.

(24) Dinnocenzo, J. P.; Schmittel, M. *J. Am. Chem. Soc.* **1987**, *109*, 1561.

(25) Dinnocenzo, J. P.; Conlon, D. A. *J. Am. Chem. Soc.* **1988**, *110*, 2324.

Inefficient kinetic competition between carbon-carbon bond cleavage ($k_{cc}$) and nonradiative decay ($k_{nr}$) accounts for the relatively low quantum yields observed for the photochemical degradation process. The next step involves loss of acetone and bimolecular electron transfer to a second Co(III) complex by **9**, which produces 1 equiv of **2** and Co(II), and **10**. Formation of **11** could occur via a migratory insertion reaction in which the amide nitrogen attacks the isocyanate carbon followed by loss of Co(II). Finally, solvolysis of **11** generates products **3** and **4**.[26]

The unique aspect of the photochemical reaction of **1** is clearly the migratory insertion reaction that leads to cyclic urea **3**. The following line of reasoning leads to the notion that the cyclization occurs within the metal complex. If the ligand becomes uncoordinated before cyclization, the amide nitrogen would become protonated under the pH conditions present in solution.[23] A protonated amide nitrogen is a very poor nucleophile and would not be competitive with the solvent for nucleophilic attack at the isocyanate carbon. Under these conditions, solvolysis of the isocyanate group would lead to formation of product **8**—however, this product is not observed in the reaction mixture.

As noted above, the cyclization reaction leading to formation of cyclic urea **3** bears a remarkable similarity to the reaction leading to hydantoin formation in the Cu(III)-peptide complexes. In addition, several studies reveal that ureas are typically formed in bimolecular reactions between metal-coordinated amides and isocyanates.[28] Apparently the similar course of the reactions for the Co(III) complex **1** and the Cu(III)-peptide complexes is due to the fact that in each case LMCT excitation leads to intraligand carbon-carbon bond cleavage and formation of an isocyanate functional group.

**Acknowledgment.** We acknowledge helpful comments from Professor Terrence Collins and John Brewer. This project was supported by Amoco Research Corp. and by the Division of Sponsored Research at the University of Florida.

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[26] Solvolysis of imide **11** may be slow at neutral pH (see ref 27); however, HPLC analysis shows unequivocally that **1** is decomposed stoichiometrically to 50% **2** and 50% **3** and that **11** is not observed. We are forced to conclude that, under the conditions of the photolysis, **11** is unstable. The decomposition of **11** may be catalyzed by Co(II).

[27] Hall, H. K., Jr.; Brandt, M. K.; Mason, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 6420.

[28] Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Halsted Press: Chichester, U.K. 1980.

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# Structure and Reactivity of a (Triphenylsilyl)rhodium(I) Compound

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Interest in transition-metal catalysis of hydrosilation[1] and silane oligomerization[2] has prompted structural studies of many silyl-transition-metal compounds,[3a] but only one structurally characterized nonbriding rhodium(I)-silyl compound has been reported.[3b] The authors of this report note the paucity of Rh(I)-Si structural studies; thus, when we had occasion to prepare the Rh-Si compound (triphenylsilyl)tris(trimethylphosphine)rhodium(I) (**1**), we thought it useful to determine its structure by X-ray diffraction.

**Scheme I**

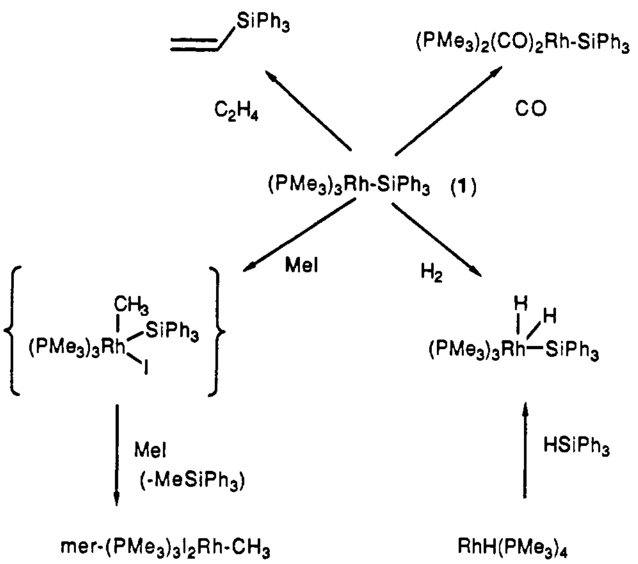
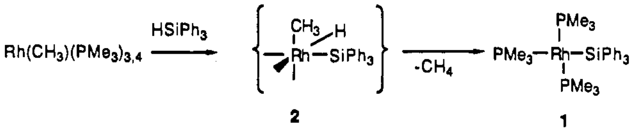


**Table I.** Selected Interatomic Distances (Å)

| | | | |
|---|---|---|---|
| Rh(1)-P(1) | 2.266 (1) | P(2)-C(5) | 1.834 (3) |
| Rh(1)-P(2) | 2.332 (1) | P(2)-C(6) | 1.828 (3) |
| Rh(1)-P(3) | 2.271 (1) | P(3)-C(7) | 1.822 (3) |
| Rh(1)-Si(1) | 2.317 (1) | P(3)-C(8) | 1.831 (3) |
| P(1)-C(1) | 1.823 (3) | P(3)-C(9) | 1.820 (3) |
| P(1)-C(2) | 1.828 (3) | Si(1)-C(11) | 1.920 (2) |
| P(1)-C(3) | 1.833 (3) | Si(1)-C(21) | 1.917 (2) |
| P(2)-C(4) | 1.827 (3) | Si(1)-C(31) | 1.913 (2) |

Compound **1** is obtained in good yield from the methane elimination reaction of eq 1.[4] The reaction is complete within



(1)

minutes at room temperature. The probable intermediate, the hydrido(methyl)(triphenylsilyl)rhodium(III) compound **2**, has not been observed, but we have characterized the iridium analogue of this putative intermediate (compound **2**-Ir) from the related reaction of $IrMe(PMe_3)_4$ with triphenylsilane. Thus compound **2**, assuming it is indeed an intermediate in the synthesis of **1**, must eliminate methane (forming the $H_3C$-H bond) much more rapidly than it eliminates methyltriphenylsilane (forming the $H_3C$-$SiPh_3$ bond). (An interesting contrast is provided by the triethylsilyl analogue of intermediate compound **2**, which eliminates methyltriethylsilane at a rate comparable to that of methane elim-

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[1] Harrod, J. F.; Chalk, A. J. In *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; John Wiley and Sons: New York, 1977; Vol. 2, pp 673-704. Speier, J. L. *Homogeneous Catalysis of Hydrosilation by Transition Metals*; Advances in Organometallic Chemistry, Vol. 17; Academic Press: New York, 1979; pp 673-704.

[2] Aitken, C. T.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059-4066.

[3] (a) See: Mackay, K. M.; Micholson, B. K. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1982; Vol. 6, Chapter 43, pp 1043-1114. See also, for example: Wang, W.-D.; Hommeltoft, S. I.; Eisenberg, R. *Organometallics* **1988**, *7*, 2417-2419. (b) Joslin, F. L.; Stobart, S. R. *J. Chem. Soc., Chem. Commun.* **1989**, 504-505. The same compound has been reported in a different space group: Oswald, A. A.; Hendriksen, D. E.; Ansell, G. B.; Zentz, S. Program and Abstracts, Combined Meeting of the 32nd Annual Denver X-ray Conference and American Crystallographic Society, Snowmass, CO, Summer 1983; p 47.

[4] Other examples of methane elimination from $MeRh(PMe_3)_3$ and reactive-hydrogen compounds have been described: Kegley, S. E.; Schaverien, C. J.; Freudenberger, J. H.; Bergman, R. G.; Nolan, S. P.; Hoff, C. D. *J. Am. Chem. Soc.* **1987**, *109*, 6563-6565. In addition, see: Schubert, U.; Müller, C. *J. Organomet. Chem.* **1989**, *373*, 165-172. Schubert, U.; Müller, J. *J. Organomet. Chem.* **1988**, *340*, 101-109.

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