Table I. Photostimulated Reaction, $RHgCl + QY \rightarrow RY + ClHgQ$

R	Q-Y	conditions[a]	RY, %[b]
$CH_2=CHCH_2CH_2$	PhS-SPh	PhH, 4 h	92
$CH_2=CHCH_2CH_2$	PhS-SPh	PhH, dark, 6.5 h, 50 °C	0
$CH_2=CHCH_2CH_2$	PhS-SPh	PhH, 4 h, 10 mol % $(Me_3C)_2NO\cdot$	0
$CH_2=CHCH_2CH_2$	PhS-SPh	PhH, AIBN, 10 h, 80 °C	64[c]
$CH_2=CHCH_2CH_2$	PhSe-SePh	PhH, 5 h	85
$CH_2=CHCH_2CH_2$	PhTe-TePh	PhH, 3 h	92
$CH_2=CHCH_2CH_2$	*p*-$MePhSO_2$-SePh	PhH, 4 h	87
$CH_3(CH_2)_4CH_2$	PhS-SPh	PhH, 3 h	78
$CH_3(CH_2)_4CH_2$	PhSe-SePh	PhH, 4 h	82
$CH_3(CH_2)_4CH_2$	PhTe-TePh	PhH, 4 h	83
$CH_3(CH_2)_4CH_2$	*p*-$MePhSO_2$-SePh	PhH, 5 h	82
$CH_3(CH_2)_4CH_2$	$PhSO_2$-Cl	PhH, 48 h[d]	46
$CH_3(CH_2)_4CH_2$	CCl_3-Br	PhH, 36 h	56
$(CH_3)_3CCH_2$	PhS-SPh	PhH, 12 h	74
$(CH_3)_3CCH_2$	PhSe-SePh	PhH, 5 h	86
$(CH_3)_3CCH_2$	PhTe-TePh	PhH, 6 h	78
$(CH_3)_3CCH_2$	*p*-$MePhSO_2$-SePh	PhH, 10 h	75
$(CH_3)_2CH$	PhS-SPh	PhH, 4 h	100
$(CH_3)_2CH$	PhSe-SePh	PhH, 5 h	100
cyclo-C_6H_{11}	PhS-SPh	Me_2SO, 18 h	65[c]
cyclo-C_6H_{11}	PhSe-SePh	Me_2SO, 16 h	72[c]
cyclo-$C_5H_9CH_2$	PhS-SPh	PhH, 4 h	86 (73[c])
cyclo-$C_5H_9CH_2$	PhSe-SePh	PhH, 4 h	84
7-norbornyl	PhS-SPh	PhH, 6 h	43[e]
7-norbornyl	PhSe-SePh	PhH, 4 h	53[e]
7-norbornyl	PhTe-TePh	PhH, 10 h	45[e]
7-norbornyl	*p*-$MePhSO_2$-SePh	PhH, 10 h	48[e]
$CH_2=CH(CH_2)_3CH_2$	PhS-S-Ph	PhH, 3 h	88[f]
$CH_2=CH(CH_2)_3CH_2$	PhSe-SePh	PhH, 3 h	93[f]
$CH_2=CH(CH_2)_3CH_2$	PhTe-TePh	PhH, 8 h	85[f]
$CH_2=CH(CH_2)_3CH_2$	*p*-$MePhSO_2$-SePh	PhH, 6 h	81[f]
$CH_2=CH(CH_2)_3CH_2$	$PhSO_2$-Cl	PhH, 48 h[d]	54[f]
$CH_2=CH(CH_2)_3CH_2$	PhS-H	PhH, 5 h	58[f]
$CH_2=CH(CH_2)_3CH_2$	PhS-H	PhH, dark, 10 mol % $(Me_3C)_2NO\cdot$, 30 °C, 38 h	0
$PhCH_2$	PhS-SPh	PhH, 4 h[d]	15 (66[g])
$PhCH_2$	PhSe-SePh	PhH, 2 h	72 (7[g])
$PhCH_2$	PhTe-TePh	PhH, 1 h	80 (0[g])
$PhCH_2$	*p*-$MePhSO_2$-SePh	PhH, 6 h	68 (5[g])
$PhCH_2$[h]	PhS-SPh	PhH, 6 h[d]	8 (72[g])
$PhCH_2$[h]	PhTe-TePh	PhH, 1 h	100 (0[g])
$CH_3CH_2CH_2CH_2$[h]	PhS-SPh	PhH, 2.5 h	100
$CH_3CH_2CH_2CH_2$[i]	PhS-SPh	PhH, 21 h	85

[a] In a typical experiment RHgCl (1 mmol) and QY (1.2 mmol) in 10 mL of solvent were irradiated with a 275-W sunlamp approximately 15 cm from the Pyrex reaction flask. The reaction temperature was ~45 °C. [b] ^1H NMR yield. [c] Isolated yield (5-mmol scale). [d] Irradiated in a Rayonet reactor (350 nm). [e] RHgBr reactant. A significant amount of RR was recovered. [f] Mixture of R = Δ^5-hexenyl and cyclopentylcarbinyl whose ratio (GLPC) was dependent on the concentration of QY. [g] Yield of $PhCH_2CH_2Ph$. [h] RHgX = R_2Hg (1 mmol); QY (2 mmol). [i] Bu_2Hg (1 mmol) and PhSSPh (1.2 mmol) yielded 1.7 mmol of PhSBu.

of PhSSPh yielded mainly $PhCH_2CH_2Ph$ and PhSHgCl while the better radical traps PhSeSePh or PhTeTePh led mainly to $PhCH_2SePh$ and exclusively to $PhCH_2TePh$ (Table I). Dibenzylmercury undergoes a facile photostimulated decomposition (inhibited by $(Me_3C)_2NO\cdot$) to $PhCH_2CH_2Ph$ and Hg^0 while $PhCH_2HgSPh$ undergoes a photostimulated chain decomposition yielding $PhCH_2CH_2Ph$, $(PhS)_2Hg$, and Hg^0. Benzylmercury chloride does not readily undergo a chain decomposition, but in the presence of anions (A^-), which promote the symmetrization to $(PhCH_2)_2Hg$ and $HgCl_2{\cdot\cdot}A^-$ ($A^- = (EtO)_2PO^-$, $ArSO_2^-$, NO_2^-), photostimulated decomposition occurs.[4] Bibenzyl could be formed in these processes by the S_H2 attack of benzyl radical at the benzyl carbon of the mercurial or by decomposition of the Hg^{III} intermediate $(PhCH_2)_2HgQ$, **1**″ (Q = $PhCH_2$, Cl, SPh, SePh, TePh). To distinguish between these alternatives, we have studied the chain reactions between $(PhCH_2)_2Hg$ and PhYYPh (Y = S, Te) in which addition of PhY· to $(PhCH_2)_2Hg$ would produce **1**″ with Q = PhS or PhTe. Reaction of 2 equiv of PhTeTePh with $(PhCH_2)_2Hg$ proceeded rapidly when photostimulated to yield quantitatively $PhCH_2TePh$ and $(PhTe)_2Hg$. We conclude that decomposition of **1**″ (Q = PhTe) leads to the benzyl radical and not directly to bibenzyl. With PhSSPh (2 equiv), a poorer trap for $PhCH_2\cdot$ than PhTeTePh, the major reaction product was $PhCH_2CH_2Ph$ (Table I). We thus conclude that bibenzyl is formed by attack of $PhCH_2\cdot$ at the benzyl position of a carbon–mercury bond with $k_6 > k_7$ for Y = S but $k_7 > k_6$ for Y = Te (Scheme I).

Scheme I

$$PhCH_2\cdot + PhCH_2HgQ \xrightarrow{S_H2} PhCH_2CH_2Ph + HgQ \quad (6)$$

$$PhCH_2\cdot + PhYYPh \rightarrow PhCH_2YPh + PhY\cdot \quad (7)$$

$$HgQ\ (Q = PhCH_2, PhY) \rightarrow Hg^0 + Q\cdot \quad (8)$$

$$HgQ + PhYYPh \rightarrow PhYHgQ + PhY\cdot \quad (9)$$

$$PhY\cdot + PhCH_2HgQ \rightarrow PhCH_2HgQYPh \quad (10)[14]$$

$$PhCH_2HgQYPh \rightarrow PhCH_2\cdot + PhYHgQ \quad (11)[14]$$

Q = $PhCH_2$, Cl, PhY (Y = S, Se, Te)

Acknowledgment. Samples of cyclopropyl- and 7-norbornylmercury bromide were kindly supplied by Professor B. Giese.[11]

Registry No. $CH_2=CHCH_2CH_2HgCl$, 14660-38-9; $CH_3(CH_2)_4CH_2HgCl$, 17774-09-3; $(CH_3)_3CCH_2HgCl$, 10284-47-6; $(CH_3)_2CHHgCl$, 30615-19-1; c-$C_6H_{11}HgCl$, 24371-94-6; c-$C_5H_9CH_2HgCl$, 33631-66-2; 7-norborrnyl HgCl, 84649-28-5; $CH_2=CH(CH_2)_3CH_2HgCl$, 63668-13-3; $PhCH_2HgCl$, 2117-39-7; PhSSPh, 882-33-7; PhSeSePh, 1666-13-3; PhTeTePh, 32294-60-3; *p*-$MePhSO_2SePh$, 68819-94-3; $PhSO_2Cl$, 98-09-9.

(14) S_H2 attack of PhY· at the carbon of $PhCH_2HgQ$ or decomposition of $PhCH_2HgQYPh$ directly to $PhCH_2HgQYPH$ are discounted because of the cyclization observed in the reactions of Δ^5-hexenylmercurials.

Iron Porphyrin Dependent Oxidation of Methyl- and Phenylhydrazine: Isolation of Iron(II)–Diazene and σ-Alkyliron(III) (or Aryliron(III)) Complexes. Relevance to the Reactions of Hemoproteins with Hydrazines

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Monosubstituted hydrazines, particularly arylhydrazines, have been shown to react with several hemoproteins such as hemoglobin[1] (Hb), myoglobin[2] (Mb), cytochrome P-450,[3] lactoperoxidase,[4] and horseradish peroxidase,[5] forming heme adducts and producing a partial inhibition or destruction of these hemoproteins.[6] The

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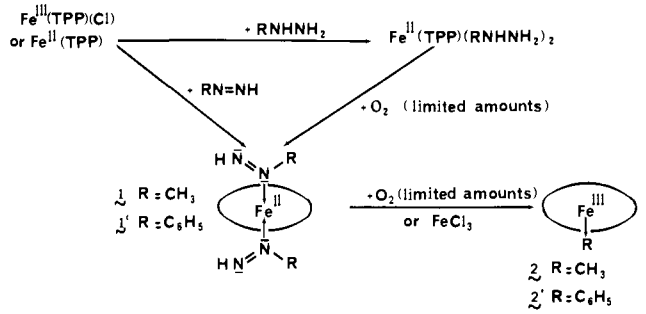
0002-7863/83/1505-1399$01.50/0

Scheme I



formation of free radicals R· has been shown during hemoprotein-catalyzed oxidation of the hydrazines $RNHNH_2$.[7,8] Intermediate formation of hemoglobin[2,9a]– and cytochrome P-450[3]–iron complexes with an oxidized metabolite of arylhydrazines has been reported, the nature of this metabolite being not yet established.[9b] Moreover, we have shown recently that the hemoglobin-dependent oxidation of methylhydrazine leads to two successive iron complexes, the first of which seems to be a hemoglobin–Fe(II)–methyldiazene complex.[10]

This communication reports preliminary results concerning a study of the reactions between iron porphyrins and hydrazines $RNHNH_2$ or diazenes RN=NH, which we have undertaken to get information on the corresponding reactions of hemoproteins and particularly on the nature of the iron complexes involved. It shows the formation of Fe(II)–diazene and σ-Fe(III)–methyl (or –phenyl) complexes upon O_2 and iron porphyrin dependent oxidation of CH_3NHNH_2 and $C_6H_5NHNH_2$ and points to very different stabilities of the complexes derived from methyl- and phenylhydrazine.

Reaction of $Fe^{II}TPP$ (TPP = mesotetraphenylporphyrin dianion) with an excess of $CH_3N{=}NH$[11] in strictly anaerobic conditions leads to the new complex **1** (Scheme I), the UV–visible spectrum (λ 424, 528, and 560 nm in CH_2Cl_2) of which is very similar to those of previously reported $Fe^{II}TPP(L)_2$ hemochrome complexes with L = amine or pyridine, for instance.[13] Upon CH_3OH addition, the crystalline complex **1** is obtained with a nearly quantitative yield. Its ^1H NMR spectrum is indicative of a diamagnetic low-spin ferrous complex with an axial symmetry: porphyrin protons at δ 8.72 (pyrrole, s, 8 H), 8.13 (*o*-phenyl, m, 8 H), and 7.71 (*m*- and *p*-phenyl, m, 12 H), involving two $CH_3N{=}NH$ axial ligands; δ −1.30 (CH_3, s, 2 × 3 H) and 7.83 (NH, s, 2 × 1 H, disappears after treatment with D_2O). Addition of pyridine-d_5 in excess at −60 °C leads to an immediate disappearance of complex **1** signals and appearance of those of $Fe^{II}TPP(pyridine\text{-}d_5)_2$ and of a singlet at δ 3.6 corresponding to the methyl protons of free $CH_3N{=}NH$,[12c] as expected for a $Fe^{II}TPP(CH_3N{=}NH)_2$ structure of complex **1**.[14] The upfield shifts observed for the $CH_3N{=}NH$ signals upon coordination to the Fe^{II}(porphyrin) ($\Delta\delta = \delta(\mathbf{1}) - \delta$(free $CH_3N{=}NH$)[12c] $\simeq$ −7.7(NH) and −4.9(CH_3)) are in the range expected for such protons in close proximity to the porphyrin plane. This structure is further supported by the presence of a band at 1510 cm^{-1} in the IR spectrum (KBr) of complex **1** as expected for $\nu_{N=N}$ of $CH_3N{=}NH$ bound to a transition metal.[16] This band disappears upon treatment of **1** with excess pyridine. **1** is highly sensitive to dioxygen either in solution or in the crystalline state.[17a] Upon exposure of crystals of **1** to dioxygen or treatment of its CH_2Cl_2 solution (10^{-3} M) by a few equivalents of O_2 or $FeCl_3$, one observes its almost quantitative conversion into a new complex exhibiting UV–visible and ^1H NMR spectra superimposable on those of an authentic sample of the σ-$Fe^{III}TPP(CH_3)$[18] complex **2**. In the crystalline state, complex **2** is more stable toward dioxygen than complex **1**, but both complexes are irreversibly transformed into $[Fe^{III}TPP]_2O$ within a few seconds in aerated benzene, explaining why opening a complex **1** solution to the air leads only very transiently to complex **2**. Reaction of $CH_3N{=}NH$ with Fe^{III}TPP(Cl) in $CDCl_3$ leads to a mixture of **1** and **2**, whose proportions are dependent on the molar excess of $CH_3N{=}NH$ used relative to FeTPP(Cl) and on O_2 traces that could be present in the medium.

Concerning CH_3NHNH_2 itself, it reduces $Fe^{III}TPP(Cl)$ (10–100 molar excess of CH_3NHNH_2) at 20 °C in anaerobic conditions, with formation of the bishydrazine hemochrome $Fe^{II}TPP(CH_3NHNH_2)_2$: Anal. $C_{46}H_{40}N_6Fe$ (C, H, N); UV–vis λ 425 nm, 532, 562. In the presence of O_2, reaction between $Fe^{III}TPP(Cl)$ and CH_3NHNH_2 leads to a mixture of $FeTPP(CH_3NHNH_2)_2$, **1**, **2**, and $[Fe^{III}TPP]_2O$,[19] the proportions of these complexes depending critically upon the FeTPP(Cl): CH_3NHNH_2:O_2 ratio. In a typical experiment, which underlines the reactions sequence shown in Scheme I, the reaction of 4 mM CH_3NHNH_2 with FeTPP(Cl), 1 mM in benzene, was followed by ^1H NMR and visible spectroscopy: $FeTPP(CH_3NHNH_2)_2$, which was first formed under argon, was rapidly oxidized upon addition of O_2 (1 mol/mol of starting hydrazine) leading predominantly to **1** and to minor amounts of **2**. Further addition of $FeCl_3$ (1.5 equiv) or of limited amounts of O_2 led to the complete transformation of **1** into **2**, whereas exposure of the solution to the air led rapidly to $[FeTPP]_2O$ and $Fe^{III}TPP(Cl)$.

Similar reactions were performed between $C_6H_5N{=}NH$[20] and $Fe^{II}TPP$ or $Fe^{III}TPP(Cl)$ and between $C_6H_5NHNH_2$ and Fe^{III}TPP(Cl) and led us to the easy isolation of the σ-phenyl complex **2'**, $Fe^{III}TPP(C_6H_5)$. It has thus been obtained in high yields ($\simeq$95%) from reaction of 8 mM $C_6H_5NHNH_2$ in CH_2Cl_2 with

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(11) $CH_3N{=}NH$ was prepared as described previously,[12] from 10^{-1} M CH_3NHOH and 10^{-1} M NH_2OSO_3H in aqueous sodium hydroxide, displaced by an argon stream and bubbled through a 10^{-3} M solution of $Fe^{II}TPP$ in CH_2Cl_2 at 20 °C.

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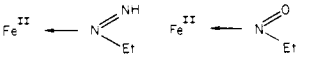
(14) Concerning the binding mode of an alkyldiazene such as $CH_3N{=}NH$ to iron, we compared the ^1H NMR spectra of $Fe^{II}TPP(EtN{=}NH)_2$, prepared by reaction of EtN=NH with $Fe^{II}TPP$, and $Fe^{II}TPP(EtNO)(py)$ (py = pyridine), prepared as described previously,[15] and found that the signals corresponding to CH_3 in bound EtN=NH and EtNO have the same chemical shift (−1.88 ppm). This is in agreement with a similar position of the methyl groups relative to the porphyrin plane in both complexes. Since RNO are bound to FeTPP by their nitrogen atom,[15b] this result would favor the Fe^{II} ← N(=NH)Et structure over the Fe^{II} ← N(=NEt)H one:



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(16) Ackerman, M. N. *Inorg. Chem.* **1971**, *10*, 272–276.

(17) (a) Because of the high sensitivity of **1** to O_2 even in the crystalline state, we were unable to get satisfactory elemental analysis for it, the samples always containing small but variable amounts of $FeTPP(CH_3)$, **2**. The mass spectrum of **1** (70 eV, 220 °C) does not exhibit the molecular peak, as most often encountered for $FeTPP(L)_2$ complexes containing weak L ligands,[17b] the highest peak being that of $FeTPP(M^+)$, *m/e* 668. (b) Budzikiewicz, H. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Volume III, p 441.

(18) (a) Lexa, D.; Mispelter, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1981**, *103*, 6806–6812. (b) Cocolios, P.; Laviron, E.; Guilard, R. *J. Organomet. Chem.* **1982**, *228*, C39–C42.

(19) As shown by ^1H NMR spectroscopy. We cannot exclude the formation of the mixed complex $Fe^{II}TPP(CH_3N{=}NH)(CH_3NHNH_2)$.

(20) $C_6H_5N{=}NH$ was prepared in CH_2Cl_2 by displacement of the $(C_6H_5N{=}NH)Cu_4Cl_4$ complex by an aqueous solution of KCN: Petridis, D.; Burke, A.; Balch, A. L. *J. Am. Chem. Soc.* **1970**, *92*, 428–429.

1 mM FeTPP(Cl) and O_2 (2 mol/mol of FeTPP(Cl)) and characterized by visible and ^1H NMR spectra superimposable on those of an authentic sample.[21] Complex **2'** is much more stable toward O_2 ($t_{1/2}$ in aerated $C_6H_6 \simeq 12$ h[21c]) than **2**. On the contrary, the diazene complex **1'**, $Fe^{II}TPP(C_6H_5N{=}NH)_2$, is much less stable than **1**; it has been only observed by visible spectroscopy (λ 426 nm, 529, 561) upon reaction of $C_6H_5N{=}NH$ with FeTPP in anaerobic conditions but could not be isolated so far because of its fast transformation into **2'** in the presence of O_2 traces. These data explain why **2'** is the main complex derived from the binding of an oxidized product of $C_6H_5NHNH_2$ to iron, observed during FeTPP and O_2-dependent oxidation of C_6H_5N-HNH_2.

The aforementioned results establish the formation of two Fe-$RNHNH_2$-derived ligand complexes upon reaction of $RNHNH_2$ hydrazines or the corresponding diazenes with an iron porphyrin and O_2 (Scheme I): an Fe(II)-diazene and a σ-Fe(III)-R complex. They show, at least when R = CH_3, that the σ-Fe(III)-R complex can be formed by a O_2-dependent oxidation of the diazene Fe(II)-$RN{=}NH$ complex. There are great similarities between these results and those concerning reactions of hemoglobin (Hb) or myoglobin (Mb) with $RNHNH_2$ (R = CH_3 or C_6H_5) and O_2:[10] when R = CH_3, two iron complexes are formed, the first one, a hemoprotein Fe(II)-$CH_3N{=}NH$ complex being further oxidized by 1 equiv of $Fe(CN)_6K_3$ (or by O_2) to give another complex, B, of unknown structure. When R = C_6H_5, the Fe(II)-$C_6H_5N{=}NH$ complex has never been observed, the only entity formed being a complex spectrally similar to B.[27] This paper describes the first isolation of a porphyriniron(II)-alkyldiazene complex[22] and points to the great instability of Fe(II)-$C_6H_5N{=}NH$ complexes, thus strongly supporting the existence of Mb- (or Hb-) Fe(II)-$CH_3N{=}NH$ complexes[10] and explaining the failure to observe Mb-Fe(II)-$C_6H_5N{=}NH$ complexes.[9a,10,23] The diazene ligands are isoelectronic with their oxygen-containing analogues, nitrosoalkanes[15] and O_2, and it is noteworthy that, as their diazene analogues, nitrosoarene-iron porphyrin complexes are considerably less stable than nitrosoalkane-iron complexes.[15c] This paper also reports for the first time the formation of σ-Fe(III)-R complexes upon reaction of $RNHNH_2$ or $RN{=}NH$ with iron porphyrins, indicating a possible $HbFe^{III}$-R (R = CH_3 or C_6H_5) structure for complexes B.[27] However, one cannot exclude presently the previously proposed[9] $HbFe^{III}$-$N{=}NR$ structure for these complexes. In that respect, it is noteworthy that hydrazines $RNHNH_2$ react with Co and Fe chelates to give Co(III)-R and Fe(III)-R σ complexes,[24] whereas $C_6H_5NHNH_2$ reacts with molybdenum porphyrins to give Mo-$N{=}NC_6H_5$ complexes.[25]

Finally, very recent preliminary results are in favor of the formation of similar iron complexes during the cytochrome P-450 dependent oxidation of CH_3NHNH_2[26] and $C_6H_5NHNH_2$.[3,26]

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(27) It was shown that an aerobic acidic treatment of this complex B' formed upon reaction of Hb with $C_6H_5NHNH_2$ leads to *N*-phenylprotoporphyrin IX.[6d,e] Since recent results showed that *N*-phenylporphyrins are formed upon similar treatment of σ-(porphyrins)Fe^{III}-C_6H_5 complexes,[28a,21c] it is tempting to propose a σ-Fe^{III}-C_6H_5 structure for the Hb complex B'.[28b]

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Organolanthanide Hydride Chemistry. 3. Reactivity of Low-Valent Samarium with Unsaturated Hydrocarbons Leading to a Structurally Characterized Samarium Hydride Complex[1]

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Our general investigation of low-valent lanthanide chemistry[3-10] has shown that the zerovalent metals react with neutral unsaturated hydrocarbons[5-10] to form a variety of new classes of organolanthanides including some that display catalytic activity.[6,7] This low-valent approach also provided the first soluble divalent organosamarium complex, $(C_5Me_5)_2Sm(THF)_2$ (I) a complex that functions as a catalyst precursor for the catalytic hydrogenation of alkynes.[10] Since I was a crystallographically characterized low-valent complex that also had catalytic chemistry, it was an ideal candidate for the study of low-valent lanthanide reactivity. We report here the reaction of I with internal alkynes to form a new class of organolanthanide complexes, the enediyls, which can be converted into the first organosamarium hydride complex, a molecule that represents a new crystallographically characterized class of organolanthanide hydrides.[11,12]

Addition of pentane to an equimolar mixture of the purple I and $C_6H_5C{\equiv}CC_6H_5$ in an inert-atmosphere glovebox immediately generates an intensely colored black solution. Removal of solvent after stirring overnight yields a black material containing unreacted alkyne by ^1H NMR spectroscopy. A pentane solution of this material precipitates the excess $C_6H_5C{\equiv}CC_6H_5$ at -78 °C, leaving a black mother liquor that is pure by ^1H NMR spectroscopy. Removal of solvent from the mother liquor leaves a black glassy material, II, which by complete elemental analysis has the formula $[(C_5Me_5)_2SmCC_6H_5]_n$ (yield >95%). The ^1H NMR and IR spectra[13] are consistent with an enediyl structure, $[(C_5Me_5)_2Sm](C_6H_5)C{=}C(C_6H_5)[Sm(C_5Me_5)_2]$, and a trans configuration is likely on the basis of steric considerations.[14]

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(13) ^1H NMR (C_6D_6) δ 1.74 (s, $C_5(CH_3)_5$), -1.26 (br s, C_6H_5), -10.15 (br s, C_6H_5) (a third broad C_6H_5 signal resolvable from the other resonances in the spectrum was not observed); ^{13}C NMR (C_6D_6) δ 123.2 (C_6H_5), 121.6 (C_6H_5), 119.4 ($C_5(CH_3)_5$), 115.3 (C_6H_5) 104.1 ($=CC_6H_5$) 19.8 ($C_5(CH_3)_5$); IR (Nujol) 3770 (w), 1670 (w), 1580 (s), 1495 (sh), 1300 (m), 1200 (w), 1160 (m), 1070 (w), 1020 (m), 975 (m), 955 (m), 750 (s), 720 (d, s), 690 (d, s), 625 (w) cm^{-1}.

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