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PC Bond Cleavage of $(silox)_3NbPMe_3$ (silox = $^tBu_3SiO$) under Dihydrogen Leads to $(silox)_3Nb{=}CH_2$, $(silox)_3Nb{=}PH$ or $(silox)_3NbP(H)Nb(silox)_3$, and CH_4

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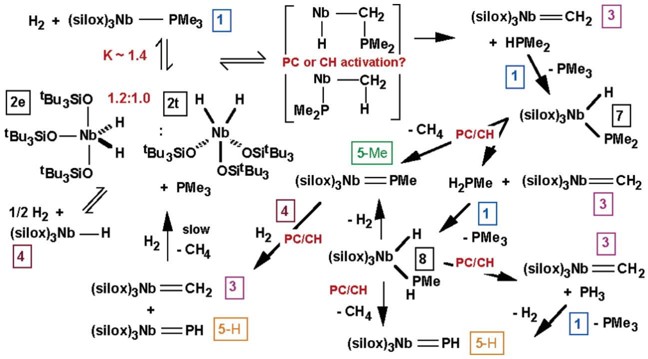
The formation of carbon−heteroatom bonds (e.g., PC bonds)[1−4] has been a focal point of organometallic reactivity studies for the past decade. Sometimes, it is also important to know how C−X bonds can be broken. Phosphorus−carbon bond cleavage, which is potentially useful with regard to the destruction of toxic agents, is often deleterious to transformations catalyzed by $((R/R')_3P)_nML_mX_o$. Substantial precedent exists for PR cleavage when R = aryl,[5−9] yet only a limited number of phosphorus−alkyl bond scissions are known,[10−15] and the majority involve chelating ligands (e.g., $Ph_2PCH_2Ph_2$).[14,15] While investigating the stability of $(silox)_3NbPMe_3$ (**1**)[16] under dihydrogen, we discovered that the PC bonds of PMe_3 were thermally severed, and that ambient light assisted the degradation. Herein we report our initial investigation of the thermal and light-dependent hydrogenation of PMe bonds.

When exposed to H_2 in hydrocarbon solvents, pseudo-T_d, indigo $(silox)_3NbPMe_3$ (**1**, $S = 1$) equilibrated ($K_{296} \sim 1.4$; $\Delta G° = -0.2$ kcal/mol) with two dihydrides, tbp $(silox)_3Nb(H_{eq})_2$ (**2e**) and pseudo-T_d $(silox)_3Nb(H_t)_2$ (**2t**), which were present in a 1.2:1.0 ratio. Scheme 1 reveals structures that are based on calculations of $(HO)_3NbH_2$ models (**2e′**, $d(NbH) = 1.78$ Å, $d(H\cdots H) = 3.11$ Å; **2t′**, $d(NbH) = 1.77$ Å, $d(H\cdots H) = 1.92$ Å), which are consistent with the rapid dissociative exchange of **2t** with H_2 ($k_f \sim 1.0(5)$ s^{-1}, $\Delta G^{‡}_{296} = 17.4(2)$ kcal/mol), and the greater width of its hydride resonance (**2t**, δ 14.08, $\nu_{1/2} \sim 160$ Hz; **2e**, δ 11.39, $\nu_{1/2} \sim 80$ Hz) in the ^1H NMR spectrum; quadrupolar broadening is expected to exert greater influence in the pseudo-cylindrically symmetric **2t**.[17]

Thermal (60 °C) degradation of **1** in the dark—with or without H_2 present—afforded ~20% magenta $(silox)_3Nb{=}CH_2$ (**3**, ^1H ($^{13}C\{^1H\}$) NMR δ_{CH_2} 9.22 (216.35), $J_{CH} = 135$ Hz), which was alternately prepared via addition of $Ph_3P{=}CH_2$ to **1**.[18] In NMR tubes in ambient light (23 °C), PC bond cleavage occurred slowly without H_2, and ~50% **3** formed over the course of 4 months along with a paramagnetic product tentatively identified as purple $(silox)_3NbH$ (**4**, $\nu(NbH/D) = 1730/1248$ cm^{-1}), which was generated independently upon hydrogenation of $(silox)_3Nb(olefin)$, ~10% $(silox)_3Nb{=}PH$ (**5**-H, ^{31}P NMR δ 515.26, $J_{PH} = 75$ Hz), and CH_4. The addition of PH_3 to **1** cleanly provided **5**-H,[9,19] which was deprotonated with $LiN(SiMe_3)_2$ to generate the yellow phosphide[20−22] $[(silox)_3NbP]Li$ (**6**, ^{93}Nb NMR δ 463, d, $J_{NbP} \sim 550$ Hz; ^{31}P NMR δ 790, m, $\nu_{1/2} \sim 5800$ Hz)[23] in useful quantities.

In NMR tubes in ambient light, solutions of **1** + $H_2 \rightleftarrows$ **2e,t** + PMe_3, which were stable in the dark at 23 °C, produced a ~4:3:1 ratio of $(silox)_3NbH$ (**4**):$(silox)_3Nb{=}CH_2$ (**3**):$(silox)_3Nb{=}PH$ (**5**-H) over 10 days along with methane. We conclude that **2e,t** has a greater light sensitivity toward PC bond cleavage than does **1**, and that its singlet excited states may be critical to facile PC activation. With a 450 W Hanovia (Hg) light source, PC bond cleavage diminished to ~15%, and ~80% **4** was generated after 3 days. Monohydride **4** appears to be thermodynamically favored, but independent reactions showed that it does not effect PC bond cleavage unless additional H_2 is present (**4** + $1/2H_2 \rightleftarrows$ **2e,t**). The **3**:**5**-H ratio suggests that, upon initial activation of PMe_3, subsequent PC bond cleavages are swift (i.e., 4 **1** → 3 **3** + **5**-H + H_2).

Scheme 1



Scale-up of the PC bond cleavage caused subtle changes in the product distribution. In a run monitored after 2 weeks, ~10% $(silox)_3Nb{=}PH$ (**5**−H) was accompanied by ~10% $(silox)_3Nb{=}PMe$ (**5**-Me, ^{31}P NMR δ 553 (br)), a green component alternatively prepared from $[(silox)_3NbP]Li$ (**6**) and MeI,[20] in addition to ~40% $(silox)_3Nb{=}CH_2$ (**3**), and $(silox)_3NbH$ (**4**, ~40%). In other reactions of 3 and 4 weeks, the **4**:**3**:**5**-H:**5**-Me ratio varied from 3:3.5:0:1.0 to 1.0:9.0:<0.5:0, respectively. Initial PC bond cleavage appears to depend on the reaction vessel (wall thickness), and thus the available UV light, but seems to be relatively insensitive to $[Nb]_{tot}$ and pH_2 (1−3 atm). In all instances, **5**-H grew in at the expense of **5**-Me, and CH_4 was produced—as much as 1.9 equiv after 2 weeks, and 2.7 equiv after 6 months according to Toepler pump measurements.

The ultimate loss of all three methyl groups from PMe_3 suggested a stepwise removal. Using the method of Abbayes et al.,[24] $HPMe_2$ and H_2PMe were prepared in situ and added to $(silox)_3NbPMe_3$ (**1**). With the former, a swift reaction afforded $(silox)_3HNbPMe_2$ (**7**), but **7** subsequently degraded ($t_{1/2} \sim 12$ h) to produce an initial ~1:1 ratio of **3**:**5**-Me and CH_4. With H_2PMe, $(silox)_3HNbPHMe$ (**8**, $t_{1/2} \sim 30$ min) was generated, but precedented H_2 loss[9,19] predominated to give **5**-Me in 60% yield, whereas PC activation occurred to a lesser extent: 20% **5**-H, 20% **3**, and CH_4. The alkylphosphide hydrides[25,26] are likely resting states preceding PC or CH bond activation, and both demethylations occur on a time scale faster than that of the initial PC/CH bond activation of PMe_3. It is tempting to conclude that the **7** → **5**-Me transformation occurs via PC bond activation to give $(silox)_3MeNbPHMe$ (**7′**) followed by 1,2-MeH elimination, but one cannot rule out rearrangement of **7** via $(silox)_3HNbCH_2PHMe \rightarrow (silox)_3(H_2MeP)Nb{=}CH_2 \rightarrow$ **7′**.

A compilation of these observations is presented in Scheme 1. Light-facilitated oxidative addition of either a PC or CH bond[27] affords transients that are subject to 1,2-$HPMe_2$ elimination and formation of $(silox)_3Nb{=}CH_2$ (**3**). The degradation of $HPMe_2$ occurs via substitution of PMe_3 from **1** (or H_2 from **2e,t**) to give

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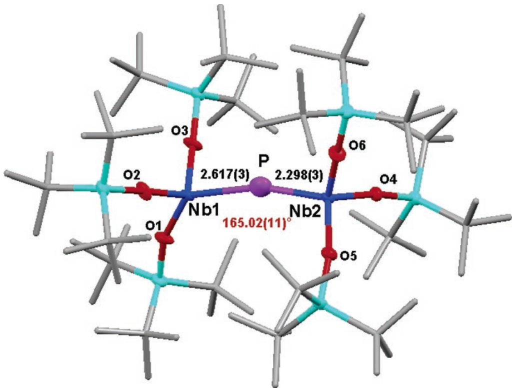

Figure 1. Molecular view and selected bond distances (Å) and angles (°) of (silox)$_3$Nb═P(H)Nb(silox)$_3$ (**9**): d(NbO)$_{av}$ = 1.904(12); O1−Nb1−O2 = 104.8(2), O1−Nb1−O3 = 102.3(2), O2−Nb1−O3 = 114.5(2), O1−Nb1−P = 135.7(2), O2−Nb1−P = 100.9(2), O3−Nb1−P = 98.9(2), O−Nb2−O$_{av}$ = 108.1(10), and O−Nb2−P$_{av}$ = 108.2(10).

(silox)$_3$HNbPMe$_2$ (**7**), which can be considered a source of (silox)$_3$NbPHMe$_2$. PC or CH bond activation and rearrangement, accompanied by 1,2-elimination of either CH$_4$ or H$_2$PMe, provides either (silox)$_3$Nb═PMe (**5**-Me) or methylene **3**. Subsequent substitutions by H$_2$PMe on **1** or **2e,t** generate (silox)$_3$HNbPMeH (**8**), a likely source of (silox)$_3$NbPH$_2$Me. Direct 1,2-elimination of H$_2$ affords **5**-Me, while another PC/CH activation step yields the methylene (**3**) and PH$_3$, thereby providing (silox)$_3$Nb═PH (**5**-H) and H$_2$ as described above. **5**-Me was independently converted by PC/CH activation to **5**-H and **3** via the addition of (silox)$_3$NbH (**4**) and H$_2$, which is a source of **2e,t**; its [Nb] dependence suggested a bimolecular PC/CH activation. Ultimately, a slow (4 weeks, 20% conversion) hydrogenation of (silox)$_3$Nb═CH$_2$ (**3**) regenerates **2e,t** along with CH$_4$, enabling hydrogenation of the remaining PMe$_3$. Surprisingly, when exposed to D$_2$, (silox)$_3$Nb═CHD (**3**-d_1) and **3**-d_2 form more swiftly (2 weeks) than reductive elimination of the putative (silox)$_3$NbD(CH$_2$D) intermediate.

When dihydrogen *and* dinitrogen (pH$_2$ ∼ pN$_2$ = 175 Torr) were added to a solution of (silox)$_3$NbPMe$_3$ (**1**) in an NMR tube under ambient light, a brick red, insoluble precipitate formed. It was identified by an X-ray crystal structure as (silox)$_3$Nb═P(H)Nb(silox)$_3$ (**9**, Figure 1). Digestion of **9** in benzene-d_6 with ethylene present provided a 1:1 mixture of (silox)$_3$Nb═PH (**5**−H) and (silox)$_3$Nb(η-C$_2$H$_4$).[28] The d(Nb^{V}P) of 2.298(3) Å is consistent with previous phosphinidenes (cf. (silox)$_3$Ta═PPh, 2.317(4) Å)[19] and is much shorter than the adjacent dative bond (d(Nb^{III}P) = 2.617(3) Å), which is considerably longer than that of **1** (2.4923(7) Å).[16] The Nb^{V} center is pseudo-T_d, with d(NbO)$_{av}$ = 1.901(8) Å, ∠ONbO$_{av}$ = 108.1(10)°, and ∠ONbP$_{av}$ = 108.2(10)°, but the Nb^{III} core exhibits a modest angular distortion of electronic origin. The existence of an insoluble P-containing species helps explain why some “solutions” appear low in **5**-H and **5**-Me with respect to **3**.

(silox)$_3$Nb═PH (**5**-H) needs to be hydrogenated or otherwise converted to regenerate **2e,t** for catalysis to occur.[29] High pressures of H$_2$ will aid in the conversion of (silox)$_3$Nb═CH$_2$ (**3**) to CH$_4$ and **2e,t**. We are currently exploring reaction conditions and the extension of these cleavage reactions to other phosphines.

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Supporting Information Available: Spectral and analytical data, CIF file for **9**, and experimental and computational procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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