acts as a trap for carbon radicals and furnishes the imines **4** with some byproduct **5**.

We suggest that this reaction involves the adduct radical **6** that is long-lived and does not react with the radical source **2**.[10] This type of dimerization of related hydrazyl radicals is known.[11] In our case **6** dimerizes to the tetraazane derivative **7**. This compound then undergoes a rearrangement with the loss of N_2 and formation of 2 mol of imine **4**.

With this reaction we have solved the problem of the transfer of a primary amino group to a carbon radical. The general usefulness of this new reaction has been demonstrated with primary, secondary, and tertiary radicals (Table I). Because of the radicophilic nature of the thiopyridone thiocarbonyl group in **2**, the formation of some of the 2-pyridyl thioether **5** is seen.

Two newer methods of carbon radical formation depend on radical exchange.[12] Thus an alcohol, converted into the corresponding aryltelluride by ionic chemistry, is radically exchanged with a methyl radical (from photoylsis of **2a**). In the second method, the alcohol is converted into xanthate (or another thiocarbonyl derivative), which then gives the desired secondary radical by reaction of the thiocarbonyl group with methyl radicals generated in the same way.[13]

The first method is illustrated in Scheme II where alcohols **8a** and **8b** were converted into the corresponding tellurides **9** and thence into **10a** (100% from the telluride **9a**) and **10b** (>95% from the telluride **9b**). We found that these imines were readily and quantitatively hydrolyzed by reflux in ethanol containing boric acid. Without the boric acid no reaction occurred.

3-Amino-3-deoxy-D-glucose is an important amino deoxy sugar found, for example, in kanamycin A. We report two new syntheses of this sugar (Scheme III). First, the glucose derivative **12** was converted to the epimer **13a** (R = H, 61%).[14] After tosylation to **13b** (R = Tos) and displacement with anisyltelluride to give **14** (35–41% **14** + the rest was recovered as **13a**), the methyl radical exchange process and reaction with **3a** gave the imine **15** (95%),[14] from which the amine **16a** (87%) was obtained.[15-17] The hydrolysis of the imine was carried out with boric acid in aqueous ethyl alcohol. Acetylation gave the known **16b** (90%).[16]

Alternately, the glucose derivative **12** was transformed to the known xanthate[2] **17** and reacted with the methyl radicals generated from **2a**. The carbon radical **18** can react with diazirine **3a** to furnish imine **15** (60%). The stereochemistry of **15** is exclusively 3β showing, once again,[18] how configuration can be determined in radical reactions simply by steric bulk, in this case that of the 1,2-acetonide group on the α-face of the five-membered ring.

Acknowledgment. Support from the National Institutes of Health and the Schering-Plough Corporation is gratefully acknowledged. E.A.T. is a Schering-Plough Scholar.

Supplementary Material Available: Experimental details and spectral data for the synthesis of compounds **14**, **15**, and **16a**,**b** (4 pages). Ordering information is given on any current masthead page.

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Reversible Uptake of H_2 and N_2 at Cobalt in the Solid State. Influence of the Counter Anion on the Formation of Classical Dihydride vs Nonclassical η^2-Dihydrogen Forms of $[(PP_3)CoH_2]^+$

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Received February 3, 1992

It has recently been reported that a variety of unexpected and intriguing reactions can occur between solid metal complexes and gaseous molecules.[1-3] Herein we report that a steady stream of H_2 (1 atm) quantitatively transforms purple-red crystals of $[(PP_3)Co(N_2)]BPh_4$ (**1**) (average crystal volume: 0.05 (1) mm^3, 200 mg, 90 °C, 1 h) into the off-white classical dihydride $[(PP_3)Co(H_2)]BPh_4$ (**2**). The reaction is reversible; i.e., by treatment of solid **2** with N_2 under identical conditions, the dinitrogen complex **1** is quantitatively regenerated (Scheme I). No fragmentation of the crystals occurs, indicating that the solid–gas reactions do not proceed by interaction of H_2 or N_2 with the surface of the crystals and are not followed by breakup of the crystal structure to facilitate further reaction. On the other hand, after a cycle of N_2/H_2 uptake, the crystals appear opaque and lose their single-crystal nature (cross-polarizing microscope). No solid–gas reaction is observed below 65 °C; above that temperature a color change shows that reaction is occurring. At 90 °C the reaction is complete in 1 h (IR, Nujol mulls; ^{31}P NMR, THF-d_8 solution). The smaller the crystal size, the faster the reaction.

An X-ray analysis has been carried out on compound **2** after recrystallization from tetrahydrofuran (THF)/ethanol to give **2**·THF.[4]

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(4) Crystal data for $C_{70}H_{72}P_4O_1B_1Co_1$: triclinic; a = 12.851 (1) Å, b = 14.541 (4) Å, c = 17.717 (2) Å, α = 107.14 (2)°, β = 105.66 (1)°, γ = 90.25 (1)° with Z = 2 in space group $P\bar{1}$; R = 0.071 and R_w = 0.072 for 5694 reflections with $F > 3\sigma(F)$ and anisotropic thermal parameters for Co, P, and B. Compounds **2** and **2**·THF exhibit quite comparable solid-state IR spectra in the ν(Co–H) region: **2** 1967, 1833 cm^{-1}; **2**·THF 1965, 1842 cm^{-1}.

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Co-P_1	2.169(2)	P_1-Co-P_2	152.54(8)
Co-P_2	2.165(2)	P_1-Co-P_3	103.08(8)
Co-P_3	2.196(2)	P_1-Co-P4	88.24(8)
Co-P_4	2.138(2)	P_2-Co-P_3	104.00(8)
Co-H_1	1.28(8)	P_2-Co-P_4	87.99(7)
Co-H_2	1.51(6)	P_3-Co-P_4	88.65(8)
		H_1-Co-H_2	88(4)

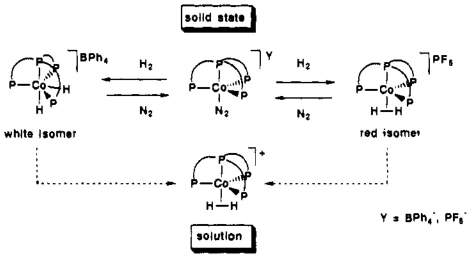
$[(PP_3)Co(H)_2)]^+ BPh_4^-$ (2·THF)

Co-P_1	2.176(5)	P_1-Co-P_2	121.1(2)
Co-P_2	2.212(5)	P_1-Co-P_3	121.6(2)
Co-P_3	2.207(4)	P_1-Co-P4	86.5(2)
Co-P_4	2.123(5)	P_2-Co-P_3	115.9(2)
		P_2-Co-P_4	86.5(2)
		P_3-Co-P_4	85.7(2)

$[(PP_3)Co(\eta^2\text{-}H_2)]^+ PF_6^-$ (4)

Figure 1. ORTEP drawings of the complex cations in **2** and **4**. Phenyl ligands have been omitted for the sake of clarity.

Scheme I



The metathetical reaction of **1** in THF with an excess of $(NH_4)PF_6$ yields $[(PP_3)Co(N_2)]PF_6$ (**3**), which maintains the trigonal bipyramidal structure of the BPh_4^- precursor in both the solid state and solution as shown by IR (Nujol mulls), diffuse reflectance, and $^{31}P\{^1H\}$ NMR (acetone-d_6) spectra.[5] Compound **3** reacts in the solid state with H_2 (200 mg, 90 °C, 1 h), converting to the red nonclassical η^2-H_2 complex $[(PP_3)Co(H_2)]PF_6$ (**4**), which has been authenticated by a single-crystal X-ray analysis[6] as well as by NMR measurements in solution.[5]

Figure 1 compares the two complex cations in the structures of **2** and **4**, respectively. Although the coordinated hydrogen atoms could be located only for **2**, geometric details leave no doubt that the two species are different. In the cation of **4**, the wrapping mode of PP_3 about the metal almost conforms to 3-fold symmetry. In fact, the angles formed at the metal by the terminal P atoms (P_t) are all close to 120°. In this case the H_2 molecule sits on the free axial position of a trigonal bipyramid. In the cation of **2**, the angle P_1–Co–P_2 is as large as 151°. The fragment $(PP_3)Co$ does not have the butterfly shape typical of L_4M fragments with C_{2v} symmetry (required P–M–P angle = 180°), but still two separate H atoms can complete a pseudo-octahedron at the metal. One hydride ligand is trans to the central P_c donor of PP_3, while the other lies along the bisector of the angle P_1–Co–P_2. The latter is sufficiently opened up to avoid short contacts of the hydride ligand with the surrounding environment.

The solid-state reactions can be monitored by IR spectroscopy (Nujol mulls) following the disappearance of the $\nu(N\equiv N)$ band in **1** and **3** (2125 cm^{-1}, s) which, in case of the classical form **2**, is replaced by two ν(Co—H) absorptions (1967 and 1833 cm^{-1}, m).

Isomers **2** and **4** are indistinguishable in solution. Indeed, the colorless classical dihydride **2** dissolves in THF, acetone, or CH_2Cl_2 under 1 atm of H_2 to give pink-red solutions of the nonclassical η^2-dihydrogen complex $[(PP_3)Co(\eta^2\text{-}H_2)]^+$ (^1H, ^{31}P NMR).[5] However, by addition of ethanol to these solutions, the classical off-white form **2** precipitates quantitatively. In contrast, solutions of the PF_6 complex **4** invariably precipitate the red nonclassical isomer unless an excess of $NaBPh_4$ is added, in which case the off-white form **2** is obtained.

Some of these results deserve comment. (1) The solid-state reactions are stoichiometric, so that all cobalt centers are accessible to H_2/N_2. (2) This is the first well-documented example of an $M(H)_2 \rightarrow M(H_2)$ tautomerization reaction which occurs on going from the solid state to solution.[7] (3) In light of the observed structural difference between the $(PP_3)Co$ fragments in the cations of **2** and in **4**, the opening of one P_t–Co–P_t angle appears to be the critical governing parameter of the dichotomy. MO calculations (to be reported elsewhere) show that the frontier FMOs of $(PP_3)Co(I)$ are dramatically affected by this latter parameter. Essentially, the z^2 (a_1, empty) and the x^2–y^2 (2e, filled) atomic orbitals of the trigonal pyramidal fragment (TP) undergo an *avoided crossing* that changes their initial nature. While the empty σ lobe of z^2 is simply reoriented in the plane perpendicular to that of the P_t–Co–P_t opening angle, a hybridized metal d_π orbital (filled) is newly formed in the same plane. In other words, the orbital conditions[8] for the oxidative addition of H_2 are initially absent (lack at the TP geometry of a metal d_π orbital with the appropriate energy and hybridization). The geometric deformation $C_{3v} \rightarrow C_s$ allows the metal to exert the strong π-back-donation that eventually leads to the H–H bond cleavage. (4) Different counter anions in the structure can affect the formation of a classical dihydride (oxidative addition) vs its nonclassical η^2-H_2 tautomer.

Acknowledgment. Thanks are due to "Progetti Finalizzati-Chimica Fine II", CNR, Rome, Italy.

Supplementary Material Available: X-ray crystallographic data for **2**·THF and **4**, including experimental details, selected bond distances and angles, atomic coordinates, and thermal parameters (11 pages); listings of observed and calculated structure factors for **2**·THF and **4** (45 pages). Ordering information is given on any current masthead page.

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