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Preliminary communication

LIGAND SCAVENGING AND CATALYTIC UTILIZATION OF THE PHOTOTRANSIENT $ReH_5(PMe_2Ph)_2$

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Summary

Photogenerated ReH_5P_2 ($P = P(CH_3)_2C_6H_5$) effects hydrogen exchange selectively at the β-carbons of naphthalene. Under one atm H_2, hex-1-ene is hydrogenated catalytically. Cyclopentene, however, forms the complex ReH_3P_3-(η^2-C_5H_8), whose crystal structure shows hydride coordinated *cis* to the olefin. Photolysis of this complex results in disproportionation of the carbocycle to yield cyclopentane, (η^5-C_5H_5)ReH_2P_2 and (η^5-C_5H_5)ReH_4P. In the presence of *t*-butylethylene as a hydrogen acceptor, ReH_5P_2 is transformed into a species which dehydrogenates cyclopentane to (η^5-C_5H_5)ReH_2P_2. Reaction of ReH_5P_2 and *t*-butylethylene in benzene solvent under N_2 yield the arene complex (C_6H_6)ReP_2($CH_2CH_2CMe_3$) and *fac*-Re($PMe_2C_6H_5$)$_3$($PMe_2C_6H_4$)N_2, whose crystal structure is reported.

Following our observation that 366 nm irradiation of ReH_5P_3 ($P = PMe_2Ph$) results in phosphine dissociation [1], we report here a broader study of the reactivity of photogenerated ReH_5P_2. Photogeneration (25°C) of ReD_5P_2 in a C_6D_6 solution in the presence of naphthalene leads to deuteration of the naphthalene. Under these circumstances, the C_6D_6 serves as a reservoir of deuterium and extensive deuteration of the naphthalene occurs in 3 h (550 W Hanovia lamp). Analysis of deuterium incorporation into recovered (sublimed) naphthalene by a combination of ^1H and ^2D NMR shows a substantial** prefer-

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* Contribution No. 3773.

** A sample enriched to 46% deuterium overall is 74% enriched at the 2,3,6,7-positions and 19% enriched at the 1,4,5,8-positions. The mass spectrum of this sample shows it to be ~12% d_0 (totally unenriched).

ence for H/D exchange at the four equivalent β-carbons of naphthalene.

Photolysis of $ReH_5(PMe_2Ph)_3$ and 1-hexene (mole ratio 1/8) in cyclohexane-d_{12} or hexafluorobenzene under 1 atm of H_2 results in complete hydrogenation of the olefin in 3 h (25°C). The reaction is catalytic in rhenium, but requires continuous photolysis: shuttering the light after an initial irradiation period of 10 min gives no significant additional hydrogenation over a dark period of 12 h.

The situation differs with internal olefins. Irradiation of ReH_5P_3 and cyclopentene (mole ratio 1/10) for 1 h in C_6H_6 results in nearly quantitative (by NMR) conversion to a stable hydridoolefin complex, $ReH_3(PMe_2Ph)_3$(cyclopentene) (I)*. No olefin hydrogenation is observed. The X-ray structure** of I has been determined using crystals grown from hexane (Fig. 1). Although the

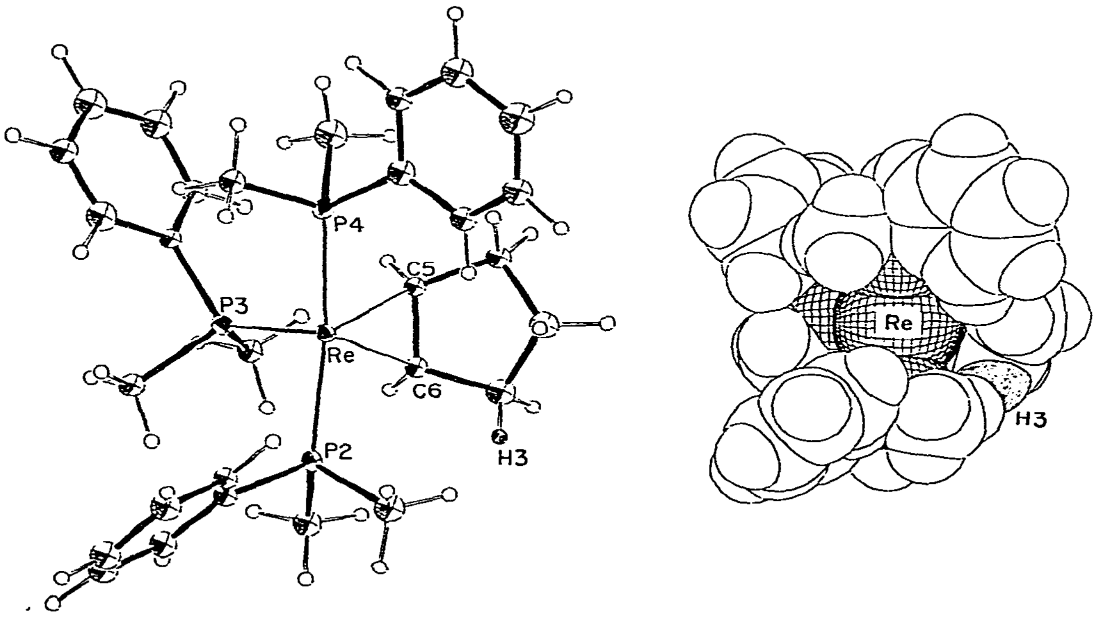

Fig. 1. Conventional ORTEP and space-filling drawings of $ReH_3(PMe_2Ph)_3(\eta^2\text{-}C_5H_8)$. In this view, the edge of the equatorial plane of a proposed pentagonal bipyramid is horizontal, and the three hydrogens bound to rhenium are proposed to project out towards the reader. These hydrogens reside in the crevice shown in the space-filling view; other views of the molecule show no channel through which the metal is visible. One of the allylic hydrogens (H(3)) of the cyclopentene ligand is densely hatched.
Selected bond lengths: Re—P(2) = 2.355(3) Å, Re—P(4) = 2.374(3) Å, Re—P(3) = 2.423(4) Å, Re—C(5) = 2.275(14) Å, Re—C(6) = 2.267(13) Å, C(5)—C(6) = 1.423(18) Å.

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*NMR data for $ReH_3(PMe_2Ph)_3(C_5H_8)$ in toluene-d_8: ^1H NMR at 220 MHz and 50°C, δ (ppm) −6.90(3), quartet, J 17 Hz, Re—H; 1.45(18), doublet, J 5 Hz, P—CH_3; 1.28(1), 2.04(3), 2.39(1), 2.68(2), all multiplets, C_5H_8; 7.59(6), broad singlet, *ortho*-C_6H_5. The *meta* and *para* protons of the phosphine overlap the protic impurity of the solvent. $^{31}P\{^1H\}$ NMR at 40.5 MHz and −70°C (chemical shifts referenced to external H_3PO_4 with downfield shifts reported as positive values) δ −14.5 ppm, doublet, J 10.3 Hz; δ −35.6 ppm, triplet, J 10.3 Hz.

**Crystallographic data (−162°C): a 16.334(5) Å, b 8.378(2) Å, c 10.739(2) Å, β 105.90(1)°, $Z = 2$ in polar space group $P2_1$; $R(F) = 0.033$, $R_w(F) = 0.033$ for 1832 observed ($F_0 > 3\sigma(F_0)$) and absorption-corrected reflections using anisotropic temperature factors for Re and three phosphorus atoms; all hydrogen atoms except those bound to Re were refined with fixed β's. A complete tabulation of crystallographic parameters is contained in Molecular Structure Center Report No. 81020, available from the Chemistry Library, Indiana University.

molecule is chiral and has no crystallographically-imposed symmetry, the coordination sphere has an approximate mirror plane of symmetry through Re, P(3), and bisecting the C=C bond of the cyclopentene. This is consistent with the AB_2 pattern seen in the $^{31}P\{^1H\}$ NMR spectrum at −70°C. Space-filling models and nonbonded contact calculations show that the (crystallographically undetected) metal-bound hydrogens must lie almost in the plane of Re, P(3), and the olefin midpoint.

Photolysis of $ReH_3P_3(C_5H_8)$ in C_6H_6 results in both hydrogenation and dehydrogenation of the C_5 ring*. $(\eta^5\text{-}C_5H_5)ReH_2P_2$ and $(\eta^5\text{-}C_5H_5)ReH_4P$ (~1/1) are detected in the ^1H NMR spectrum along with cyclopentane. The identity of these cyclopentadienyl hydride complexes has been established by ^1H NMR chemical shifts and integrations and by the multiplet patterns observed in the ^1H and selectively decoupled ^{31}P NMR spectra**.

$CpReH_4(PMe_2Ph)$ can be isolated in 20% yield after photolysis of ReH_5P_3 and cyclopentadiene in hexane (1 h at 20°C), with $CpReH_2P_2$ also being formed as a minor product. This chemistry bears a striking similarity to that recently reported by Baudry and Ephritikhine [3], who found that refluxing $ReH_7(PPh_3)_2$ in THF in the presence of cyclopentadiene produces exclusively $CpReH_2(PPh_3)_2$. Although those authors postulate that $ReH_5(PPh_3)_2$ is an intermediate in their thermal reactions, the product distribution of $\eta^5\text{-}C_5H_5$ complexes clearly differs from that obtained with our photogenerated ReH_5P_2***. Since we have shown that $CpReH_4(PMe_2Ph)$ fails to react with 3.5 equivalents of PMe_2Ph in 10 h at 70°C, we are observing a kinetically-controlled product distribution. We conclude that ReH_5P_2, either thermally generated from ReH_7P_2 or photogenerated from ReH_5P_3, reacts with the diene C_5H_6 in a stepwise manner, whose later steps exhibit considerable thermal control:

$$\begin{tikzcd}
\mathrm{ReH_5P_2} + \mathrm{C_5H_6} \arrow[r] & \mathrm{ReH_5P_2(\eta^2\text{-}C_5H_6)} \arrow[dl] \arrow[dr] & \\
(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{ReH_2P_2} + 2\mathrm{H_2} & & (\eta^5\text{-}\mathrm{C_5H_5})\mathrm{ReH_4P} + \mathrm{H_2} + \mathrm{P}
\end{tikzcd}$$

Since Crabtree [4] and later Ephritikhine et al. [5] have shown that t-butylethylene can markedly influence hydrogen transfer reactivity, we explored the effect of this olefin on our photosystem. The most dramatic influence we have encountered occurs in cyclopentane. Irradiation of ReH_5P_3 in pure cyclopentane yields $Re_2H_6P_5$, the product of scavenging of ReH_5P_2 by ReH_5P_n in an otherwise unreactive environment [1]. If the same experiment is repeated

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*Pt/Re catalysts are widely employed in hydrocarbon reforming (disproportionation) [2].

**NMR data for $CpReH_4PMe_2Ph$ in C_6D_6: ^1H NMR at 60 MHz and 35°C, δ (ppm) −8.4 [4], doublet, J 20 Hz, Re—H; 1.72(6), doublet, J 10 Hz, P—CH_3; 4.24(5), broad singlet, C_5H_5; 6.9—7.6, multiplet, C_6H_5. The $^{31}P\{^1H\}$ spectrum is a singlet at δ −17.5 ppm which becomes a quintet upon selective decoupling of the downfield protons.

NMR data for $CpReH_2(PMe_2Ph)_2$ in C_6D_6: ^1H NMR at 60 MHz and 35°C, δ (ppm) −11.5(2), triplet, J 42.5 Hz, Re—H; 1.72(12), doublet, J 10 Hz, P—CH_3; 4.39(5), singlet, C_5H_5; 7.1—7.7, multiplet, C_6H_5. The $^{31}P\{^1H\}$ spectrum is a singlet at δ −17.5 ppm which becomes a triplet upon selective decoupling of the downfield protons.

***We have established that the identity of the phosphine does not alter this conclusion. A hexane solution of $ReH_7(PMe_2Ph)_2$ and cyclopentadiene heated to 70°C for twenty minutes produces only $CpReH_2(PMe_2Ph)_2$. Also, photolysis of $ReH_5(PPh_3)_3$ and cyclopentadiene in THF cleanly produces $CpReH_4(PPh_3)$; no $CpReH_2(PPh_3)_2$ is detected.

with 8 volume percent t-butylethylene added to the cyclopentane, (η^5-C_5H_5)-ReH_2P_2 is produced (unoptimized yield: 5%). No other cyclopentadiene or hydride-containing products and no rhenium metal are detected in the resulting yellow-brown homogeneous solution. We conclude that ReH_5P_2 is incapable of reacting with cyclopentane, but that t-butylethylene dehydrogenates this phototransient to a species sufficiently devoid of ligands and sufficiently electron rich to react with the C—H bonds of cyclopentane.

We have exploited this "hydride-stripping" capacity of t-butylethylene to produce arene-rhenium complexes, something which our earlier work showed was not possible directly from ReH_5P_2. Irradiation of a benzene solution of ReH_5P_3 and t-butylethylene (mole ratio 1/16) in a stoppered NMR tube under 1 atm N_2 results in hydrogenation of the olefin and a mixture of rhenium products. The arene complex we sought is indeed produced; (η^6-C_6H_6)ReP_2-($CH_2CH_2CMe_3$) has appropriate ^1H NMR resonances*, as does the analogous π-toluene complex from toluene solvent. However, the identity of the other product was not established until the X-ray structure** (Fig. 2) was complete. The product is *fac*-Re(PMe_2Ph)$_3$($PMe_2C_6H_4$)N_2***, resulting from the complete loss of Re—H ligands and the loss of one aryl *ortho* hydrogen upon *ortho*-metallation. This is a rare instance [6] where an arylphosphine with a cone angle as small as dimethylphenylphosphine has undergone *ortho*-metallation and contrasts with our observation that ReD_5P_2 undergoes no H/D exchange at the *ortho*-positions. This emphasizes the high reactivity of intermediates produced using t-butylethylene. Most remarkable is the fact that this reaction

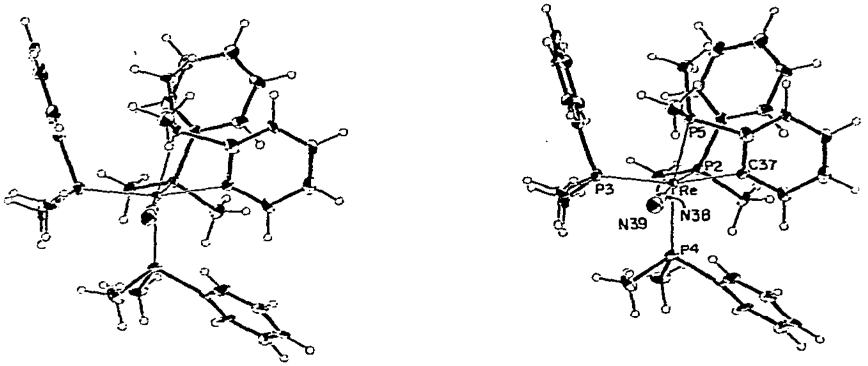

Fig. 2. ORTEP drawing of *fac*-$ReN_2(PMe_2Ph)_3(PMe_2C_6H_4)$.
Selected structural data: Re—P(2) = 2.395(3) Å, Re—P(3) = 2.362(3) Å, Re—P(4) = 2.357(3) Å, Re—P(5) = 2.419(3) Å, Re—C(37) = 2.203(12) Å, Re—N(38) = 1.960(10) Å, N(38)—N(39) = 1.117(13) Å. Angle Re—N(38)—N(39) = 178.2(10)°, angle P(5)—Re—C(37) = 65.6(3)°.

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*^1H NMR at 220 MHz and 16°C: δ (ppm) 4.07(6), singlet, C_6H_6; 1.18(9), singlet, $C(CH_3)_3$.

**Crystallographic data (−160°C): a 19.494(7) Å, b 10.403(2) Å, c 18.772(7) Å, β 120.64(2)°, $Z = 4$ in space group $P2_1/a$; $R(F) = 0.061$, $R_w(F) = 0.054$ for 4236 observed ($F_o > 2.33\sigma(F_o)$) reflections using anisotropic temperature factors for all nonhydrogen atoms. Placing hydrogen atoms in calculated positions reduced the residuals to 0.056 and 0.047, respectively. A complete tabulation of crystallographic parameters appears in Molecular Structure Center Report No. 81026, available from the Chemistry Library, Indiana University.

***$^{31}P\{^1H\}$ NMR at 40.5 MHz (referenced as above): δ −88.6 ppm, doublet (J 160 Hz) of pseudotriplets (J 20 Hz), P(5); δ −25.7 ppm, complex multiplet, P(2) (or P(3)) and ½P(4); δ −30.5 ppm, complex multiplet, P(3) (for P(2)) and ½P(4). ν(NN) 2000 cm^{-1} (Nujol).

system (overall phosphine/Re ratio = 3/1) becomes so deficient of ligands that dinitrogen is scavenged to play this role. Our results also demonstrate that dinitrogen (~5 × 10^{-3} *M*) [7] is a superior ligand to the abundantly available t-butylethylene (7 × 10^{-1} *M*).

It is clear that ligand photodissociation from $ReH_5(PMe_2Ph)_3$ provides access to a transient of high and diverse reactivity, and one which readily shuttles between many oxidation states.

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