ORGANOMETALLICS

Volume 4, Number 7, July 1985

© Copyright 1985
American Chemical Society

Selective Hydrogenation of Acenaphthylene by $ReH_7(PCy_3)_2$

David G. DeWit, Kirsten Folting, William E. Streib, and Kenneth G. Caulton*

Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405

Received October 31, 1984

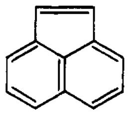
Acenaphthylene ($C_{12}H_8$) reacts with $ReH_7(PCy_3)_2$ (Cy = cyclohexyl) at 70 °C to give a complex shown by ^1H and ^{31}P NMR and X-ray crystallography to be $(\eta^4\text{-}C_{12}H_{10})ReH_3(PCy_3)_2$. The molecule adopts a distorted pentagonal-bipyramidal structure with rhenium bound to four carbons of one six-membered ring. This compound is stereochemically rigid, showing three inequivalent hydride and two inequivalent phosphorus nuclei. Since the hydrocarbon ligand has had one double bond hydrogenated (the one not involved in the naphthalene framework) and since this ligand is not displaced by $C_{12}H_8$ under the reaction conditions, the hydrogenation appears to proceed by intramolecular hydrogen transfer. Crystal data (−158 °C): $a = 18.920$ (6) Å, $b = 12.976$ (3) Å, $c = 18.685$ (6) Å, $\beta = 111.63$ (1)°, and $Z = 4$ in space group $P2_1/c$.

Introduction

The rhenium polyhydrides $ReH_7(PAr_3)_2$ (Ar = Ph, *p*-tolyl, *p*-FC_6H_4), in the presence of *tert*-butylethylene, have been shown to dehydrogenate cycloalkanes and *n*-pentane.[1-3] The *tert*-butylethylene is thought to function to strip hydrogen ligands from rhenium, thereby creating a highly unsaturated metal center; no attack on hydrocarbon has been reported in the absence of *tert*-butylethylene. It has been proposed[1] that this reaction is initiated by thermal reductive elimination of H_2, to generate the 16-electron species $ReH_5(PAr_3)_2$. We have shown independently that unsaturated $ReH_5(PMe_2Ph)_2$ can be generated by photolysis of $ReH_5(PMe_2Ph)_3$ and that this species effects H/D exchange with C_6H_6;[4,5] in the presence of *tert*-butylethylene, this phototransient dehydrogenates cyclopentane to give $(\eta^5\text{-}C_5H_5)ReH_2(PMe_2Ph)_2$.[6]

In an effort to understand how the phosphine ligand might influence these hydrocarbon modification reactions, we have synthesized $ReH_7(PCy_3)_2$ (Cy = cyclohexyl) and have shown (by kinetic and D_2 scavenging methods) that it participates (above 50 °C) in a reductive elimination equilibrium (eq 1) leading again to a pentahydride bis(phosphine) complex.[7] This pentahydride is trapped by

$$ReH_7(PCy_3)_2 \rightleftharpoons ReH_5(PCy_3)_2 + H_2 \qquad (1)$$



I

other phosphine ligands L (to give $ReH_5(PCy_3)_2L$), but also (by the same mechanism) by acenaphthylene, I. In the case of acenaphthylene, the isolated product is not a pentahydride (as in the case of phosphorus nucleophiles), but a trihydride with two inequivalent phosphine ligands and three inequivalent hydrides: $(\eta^4\text{-}C_{12}H_n)ReH_3(PCy_3)_2$.[7] At the time of our kinetic studies, we were uncertain of the number of hydrogens, *n*, on the C_{12} hydrocarbon (i.e., whether or not the bound hydrocarbon had been hydrogenated, and to what extent). Also unknown was the region of the C_{12} hydrocarbon to which the metal was attached, although η^4 binding was deduced on the basis of the 18-electron rule. It was to establish these features (of obvious relevance to the question of how *tert*-butylethylene acts to dehydrogenate $ReH_7(PRe)_2$,[1-3,6] and also to understand the origin of the low molecular symmetry (all hydrides and both phosphorus nuclei inequivalent by NMR) and implied stereochemical rigidity of the product, that the work reported here was undertaken.

Experimental Section

General Data. All manipulations were carried out under N_2 with use of standard Schlenk and glovebox techniques. Solvents were dried with Na/K alloy. ^1H NMR spectra were recorded at 360 MHz (Nicolet NT-360) and ^{31}P NMR spectra at 40.5 MHz

---

[1] Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1980**, 1243.

[2] Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1982**, 606.

[3] Baudry, P.; Ephritikhine, M.; Felkin, H.; Zakrzewski, J. *J. Chem. Soc., Chem. Commun.* **1982**, 1235.

[4] Green, M. A.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 695.

[5] Muralidharan, S.; Ferraudi, G.; Green, M. A.; Caulton, K. G. *J. Organomet. Chem.* **1983**, *244*, 47.

[6] Green, M. A.; Huffman, J. C.; Caulton, K. G.; Rybak, W. K.; Ziolkowski, J. J. *J. Organomet. Chem.* **1981**, *218*, C39.

[7] Zeiher, E. H. K.; DeWit, D. G.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 7006.

0276-7333/85/2304-1149$01.50/0 © 1985 American Chemical Society

Table I. Crystal Data for (η^4-$C_{12}H_{10}$)$ReH_3(PCy_3)_2$

formula	$C_{48}H_{79}P_2Re$
color	yellow
cryst dimens, mm	0.10 × 0.12 × 0.11
space group	$P2_1/c$
cell dimens (at −158 °C; 30 reflctns)	
a, Å	18.920 (6)
b, Å	12.976 (3)
c, Å	18.685 (6)
β, deg	111.63 (1)
molecules/cell	4
vol, Å^3	4264.27
D(calcd), (g/cm^3)	1.409
wavelength, Å	0.710 69
mol wt	904.30
linear abs coeff, cm^{-1}	29.9
max abs	0.5240
min abs	0.6160
no. of unique intensities	5589
no. with $F > 0.0$	5218
no. with $F > 3.0\sigma(F)$	4707
final residuals	
$R(F)$	0.0613
$R_w(F)$	0.0640
goodness of fit for the last cycle	1.36
max Δ/σ for last cycle	0.05

(Varian XL-100). Chemical shifts downfield of the reference (85% H_3PO_4 for phosphorus) are uniformly recorded as positive. Preparation of $ReH_7(PCy_3)_2$ has been reported.[7]

Preparation of (η^4-$C_{12}H_{10}$)$ReH_3(PCy_3)_2$. A solution containing 0.150 g (0.199 mmol) of $ReH_7(PCy_3)_2$ and 0.300 g (1.97 mmol) of acenaphthylene in 5 mL of cyclohexane was heated under N_2 for 10 h at 70 °C, whereupon the color of the solution changed from yellow to red-brown. The solution was reduced in volume to ca. 2 mL and filtered. Addition of 6 mL of ethanol to the filtrate resulted in a yellow-orange precipitate upon cooling overnight at −30 °C. The crude product was filtered and dried under a stream of N_2; considerable decomposition appeared to occur after extended exposure to vacuum, accompanied by sublimation of solid hydrocarbon. Pure product (0.065 g, 35%) was obtained by recrystallization from benzene/ethanol. Yellow-orange crystals suitable for X-ray diffraction were formed by vapor diffusion of ethanol into a benzene solution at 25 °C. ^1H NMR (360 MHz, in C_6D_6): $C_{12}H_{10}$ hydrogens, δ 6.67 and 6.60 (complex multiplet, 3 H), 4.96 (d, J = 9 Hz, 1 H), 4.80 (br, 1 H), 3.24 (complex and asymmetric multiplet, 2 H), 2.99 (complex multiplet, 2 H), 2.54 (t, J = 9 Hz, 1 H); C_6H_{11} hydrogens, δ 2.43, 1.77, 1.27, all broad; Re hydrogens, δ −6.41 (v br, 1 H), −6.89 (br, 1 H), −8.33 (br, 1 H); $^{31}P\{^1H\}$ NMR δ 27.1 (d), 21.5 (d), line spacing 58 Hz.

$ReH_7(PCy_3)_2$ + 2-Vinylnaphthalene. $ReH_7(PCy_3)_2$ (0.0282 g) and 2-vinylnaphthalene (0.0624 g) were combined in 0.6 mL of toluene and sealed in an NMR tube under vacuum. The sample was heated at 73 °C for 3 h, to give 88% conversion to an AB $^{31}P\{^1H\}$ NMR pattern with the taller peaks at 25.9 and 21.7 ppm; all four peaks are broadened. At 73 °C, the spectrum has collapsed to a singlet at 23.7 ppm, while at −15 °C the line broadening has disappeared, and the spectrum reveals an AB pattern with taller peaks at 26.3 and 21.2 ppm; each doublet has a splitting of 46 Hz.

$ReH_7(PCy_3)_2$ + 1,3-Cyclohexadiene. The rate of this reaction (disappearance of $ReH_7(PCy_3)_2$ using ^{31}P NMR) was established in a manner identical with the kinetic studies reported previously.[7]

X-ray Diffraction. A suitable small crystal was cleaved from a larger crystal, transferred to the goniostat, and characterized in our usual manner.[8] A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections which corresponded to the monoclinic space group $P2_1/c$. Characteristics of the crystal, data collection (6 ≤ 2θ ≤ 45°, −158 °C), and refinement are shown in Table I. The structure was solved by using a combination of direct methods and heavy-atom Fourier methods on reflections having $F > 3\sigma(F)$. The data were corrected for absorption. While rhenium and the PCy_3 ligands refined well, anisotropic refinement of the acenaphthene carbons led to several abnormal distances, angles, and thermal ellipsoids. Numerous attempts to find a satisfactory model for the apparent disorder were unsuccessful, even after calculating a difference Fourier map following inclusion of cyclohexyl hydrogen atoms in calculated positions and establishing that no reflections suffered from extinction. The final model chosen involved isotropic refinement of these 12 acenaphthene carbons; no hydride atoms were located. A final difference map contained four peaks in the vicinity of the acenaphthene ligand, at approximately 1.5 e/Å^3.

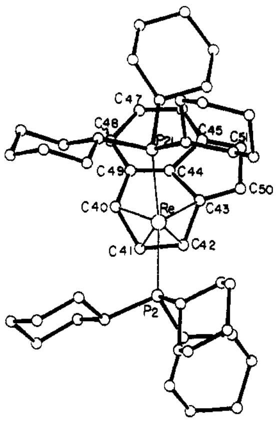


Figure 1. ORTEP drawing of the non-hydrogen atoms in (η^4-$C_{12}H_{10}$)$ReH_3(PCy_3)_2$, showing atom labeling of acenaphthene carbons. The idealized symmetry axis of a pentagonal bipyramid lies vertically (P(21)–Re–P(2)) in this view. The three hydride ligands are proposed to project toward the viewer in the horizontal plane containing Re.

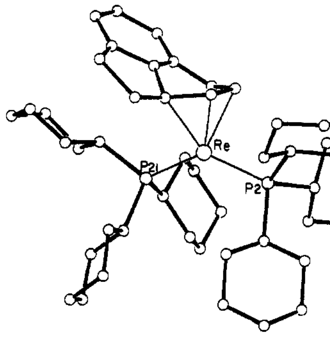


Figure 2. An alternative view of the non-hydrogen atoms in (η^4-$C_{12}H_{10}$)$ReH_3(PCy_3)_2$, showing the fold in the acenaphthene ligand.

The results of the structural study are shown in Tables II and III and Figures 1 and 2. Distances and angles within the cyclohexyl rings, thermal parameters, and observed and calculated structure factors are available as supplementary material. Cyclohexyl carbon–carbon distances attached to P2 average 1.522 Å, while those on P21 average 1.524 Å; shortest and longest C–C distances are 1.472 (19) and 1.553 (17) Å, respectively.

Results

Synthesis and Characterization. Reaction of $ReH_7(PCy_3)_2$ with excess acenaphthylene at 70 °C gives (^{31}P NMR) clean conversion to a single metal complex in less than 10 h. Consistent with the absence of a ^{31}P NMR resonance for free PCy_3, the metal complex is identified as a bis(phosphine) complex by its AB pattern in the $^{31}P\{^1H\}$ NMR spectrum. This pattern shows no evidence of coalescence at +70 °C. The isolated complex displays three broad (unstructured) hydride resonances of equal intensity, identifying it as a trihydride complex. Clearly a complex of low symmetry is indicated by these data, and this asymmetry must originate in the four-electron donor hydrocarbon ligand L in the $LReH_3(PCy_3)_2$ formula. The low molecular symmetry is also evident in the ^1H NMR of the coordinated C_{12} hydrocarbon. The arene hydrogens

---

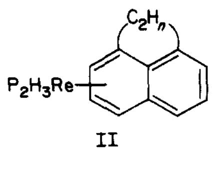
(8) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

Table II. Fractional Coordinates and Isotropic Thermal Parameters[a] for $(\eta^4\text{-}C_{12}H_{10})ReH_3(PCy_3)_2$

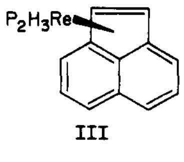
atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Re(1)	2085.7 (3)	4438.7 (3)	9829.0 (3)	32
P(2)	2554 (2)	2963 (2)	10657 (2)	27
C(3)	2856 (6)	3223 (8)	11709 (6)	29
C(4)	3562 (6)	3928 (9)	12042 (6)	35
C(5)	3776 (7)	4048 (9)	12907 (6)	40
C(6)	3133 (7)	4473 (9)	13118 (7)	41
C(7)	2443 (7)	3777 (8)	12792 (7)	38
C(8)	2202 (6)	3679 (8)	11923 (6)	31
C(9)	1863 (6)	1881 (8)	10519 (6)	29
C(10)	1945 (6)	1123 (8)	11184 (6)	33
C(11)	1264 (7)	420 (8)	10962 (7)	38
C(12)	1115 (7)	−162 (8)	10236 (7)	41
C(13)	1061 (7)	553 (10)	9575 (7)	46
C(14)	1751 (6)	1261 (9)	9776 (6)	37
C(15)	3448 (6)	2377 (9)	10635 (6)	37
C(16)	3767 (6)	1469 (8)	11181 (6)	35
C(17)	4574 (9)	1219 (12)	11269 (9)	66
C(18)	4684 (8)	1064 (11)	10537 (8)	55
C(19)	4346 (7)	1961 (10)	9979 (6)	43
C(20)	3512 (8)	2204 (11)	9881 (7)	52
P(21)	2620 (2)	5885 (2)	9378 (2)	29
C(22)	3380 (6)	5462 (8)	9021 (6)	33
C(23)	3149 (7)	4632 (8)	8386 (6)	34
C(24)	3852 (6)	4169 (8)	8322 (6)	34
C(25)	4316 (7)	4989 (9)	8105 (6)	36
C(26)	4534 (7)	5859 (8)	8703 (6)	35
C(27)	3842 (6)	6299 (8)	8818 (6)	34
C(28)	3172 (6)	6789 (9)	10170 (6)	32
C(29)	3908 (6)	6384 (8)	10751 (7)	34
C(30)	4311 (7)	7211 (10)	11339 (7)	45
C(31)	3823 (7)	7625 (10)	11741 (7)	42
C(32)	3084 (8)	8046 (10)	11166 (7)	50
C(33)	2668 (6)	7217 (9)	10595 (6)	36
C(34)	1994 (6)	6822 (9)	8643 (6)	35
C(35)	2263 (7)	7952 (8)	8710 (7)	41
C(36)	1649 (7)	8616 (9)	8129 (7)	44
C(37)	1491 (7)	8262 (10)	7323 (8)	49
C(38)	1222 (7)	7141 (10)	7211 (7)	44
C(39)	1805 (7)	6451 (8)	7807 (6)	38
C(40)	1141 (9)	5461 (12)	10061 (9)	62 (3)
C(41)	1038 (8)	4313 (11)	10080 (8)	56 (3)
C(42)	946 (8)	3778 (12)	9412 (9)	56 (3)
C(43)	971 (8)	4416 (11)	8767 (8)	53 (3)
C(44)	569 (8)	5473 (11)	8803 (8)	52 (3)
C(45)	105 (9)	5674 (13)	7938 (9)	64 (4)
C(46)	−307 (8)	6605 (11)	7830 (8)	56 (3)
C(47)	−205 (8)	7172 (11)	8466 (8)	58 (3)
C(48)	291 (9)	6922 (13)	9288 (10)	71 (4)
C(49)	676 (9)	6010 (13)	9389 (9)	69 (4)
C(50)	787 (10)	4096 (14)	8032 (10)	79 (4)
C(51)	152 (11)	4972 (15)	7478 (11)	86 (4)

[a] Isotropic values given for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

show no evidence for symmetry; at least seven chemical shifts are resolved at 360 MHz. The outstanding question at this point is the nature of the η^4 binding of Re to the C_{12} hydrocarbon (II or III), and indeed the question of



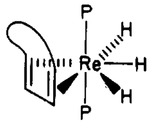
II



III

whether this hydrocarbon has been hydrogenated (n = 4, acenaphthene) or not (n = 2, acenaphthylene). Given the low symmetry of this molecule, a crystal structure determination was deemed the most direct route to resolving this question.

Molecular Structure. The structural study (Figures 1 and 2) reveals the predicted η^4 binding of rhenium to the C_{12} hydrocarbon. The orientation of the C_{12} moiety (Figure 1) makes the two phosphine ligands inequivalent (seen by ^{31}P NMR and also in the extremely complex pattern of the cyclohexyl hydrogens in the ^1H NMR). Likewise, the binding of the metal to the diene fragment of the naphthalene skeleton destroys any symmetry of the C_{12} hydrocarbon. While the X-ray study did not permit location of hydride positions, there is a large fan-shaped hole in the coordination sphere in a plane perpendicular to the Re–P(2)–P(21) plane (Figures 1 and 2), and it is here that the hydrides must lie. This, together with the assignment of two coordination positions to the diene fragment, gives coordination number 7 to Re and confirms the idea[9] that (diene)ReH_3P_2 complexes may be thought of as pentagonal bipyramidal (IV). The choice of this polyhedron is particularly compelling in that it explains the orientation of the C_{12} fragment relative to the ReP_2 unit. Finally, the C_2 fragment connecting two of the peri carbons in the C_{12} hydrocarbon destroys the molecular mirror plane which might have existed through Re, P(2), and P(21), thus making all hydrides inequivalent. The angle P(2)–Re–P(21) is of course not 180° (Figure 2) as it would be in a true pentagonal bipyramid. This bending (to 137.3°) is surely in response to repulsion between the C_{12} fragment and the phosphines. The cyclohexane rings are all in chair conformations, and the phosphorus substituent of each is equatorial.



IV

Table III. Selected Bond Distances (Å) and Angles (deg) for $(\eta^4\text{-}C_{12}H_{10})ReH_3(PCy_3)_2$

Bond Distances

Re–P(2)	2.415 (3)	C(46)–C(45)	1.411 (20)
Re–P(21)	2.426 (3)	C(44)–C(43)	1.582 (19)
Re–C(43)	2.302 (14)	C(44)–C(49)	1.250 (19)
Re–C(40)	2.389 (15)	C(44)–C(45)	1.551 (20)
Re–C(41)	2.205 (15)	C(43)–C(42)	1.477 (19)
Re–C(42)	2.180 (15)	C(43)–C(50)	1.352 (21)
P(2)–C(3)	1.864 (10)	C(40)–C(41)	1.504 (19)
P(2)–C(9)	1.870 (11)	C(40)–C(49)	1.429 (21)
P(2)–C(15)	1.869 (11)	C(41)–C(42)	1.384 (19)
P(21)–C(22)	1.877 (11)	C(47)–C(48)	1.511 (20)
P(21)–C(28)	1.875 (11)	C(49)–C(48)	1.366 (21)
P(21)–C(34)	1.889 (11)	C(45)–C(51)	1.278 (22)
C(46)–C(47)	1.350 (19)	C(51)–C(50)	1.700 (25)

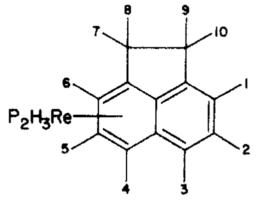
Bond Angles

P(2)–Re–P(21)	137.27 (10)	C(44)–C(43)–C(42)	106.9 (12)
Re–P(2)–C(3)	115.5 (3)	C(44)–C(43)–C(50)	111.2 (13)
Re–P(2)–C(9)	115.8 (3)	C(42)–C(43)–C(50)	125.6 (14)
Re–P(2)–C(15)	115.4 (3)	C(41)–C(40)–C(49)	118.1 (14)
C(3)–P(2)–C(9)	102.0 (4)	C(40)–C(41)–C(42)	116.7 (13)
C(3)–P(2)–C(15)	99.7 (5)	C(46)–C(47)–C(48)	127.7 (14)
C(9)–P(2)–C(15)	106.5 (5)	C(43)–C(42)–C(41)	115.1 (13)
Re–P(21)–C(22)	111.7 (3)	C(44)–C(49)–C(40)	109.8 (15)
Re–P(21)–C(28)	113.1 (3)	C(44)–C(49)–C(48)	117.2 (16)
Re–P(21)–C(34)	121.4 (3)	C(40)–C(49)–C(48)	132.7 (16)
C(22)–P(21)–C(28)	100.8 (5)	C(46)–C(45)–C(44)	111.4 (14)
C(22)–P(21)–C(34)	106.7 (5)	C(46)–C(45)–C(51)	133.3 (17)
C(28)–P(21)–C(34)	100.8 (5)	C(44)–C(45)–C(51)	115.3 (16)
C(47)–C(46)–C(45)	116.6 (14)	C(47)–C(48)–C(49)	115.2 (15)
C(43)–C(44)–C(49)	126.6 (14)	C(45)–C(51)–C(50)	106.1 (16)
C(43)–C(44)–C(45)	101.4 (11)	C(43)–C(50)–C(51)	105.8 (14)
C(49)–C(44)–C(45)	131.7 (15)		

---

(9) Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Organomet. Chem.* **1982**, *224*, 363.

Table IV. ^1H NMR of the C_{12} Ring Hydrogens in $(\eta^4\text{-}C_{12}H_{10})ReH_3(PCy_3)_2$



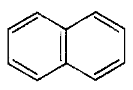
δ	intensity	suggested assignmt
6.67 6.60	3	1–3
4.96 (d, J = 9 Hz)	1	6
4.80	1	5
3.24	2	7, 8
2.99	2	9, 10
2.54 (t, J = 9 Hz)	1	4

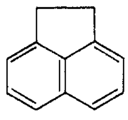
The C_{12} moiety in this trihydride showed evidence of disorder of the eight carbons not bound directly to rhenium. This takes the form of a small (<50%) population of two carbons (numbered 50 and 51) to the opposite side of the naphthalene fragment (i.e., attached to C(40) and C(48)). Associated with this second form is a minor rotation about the Re–diene vector, which gave unrealistic form to the vibrational ellipsoids of certain carbons of the C_{12} ring. A related problem has been reported for $(\eta^4\text{-}$cyclohexadiene$)ReH_3(PPh_3)_2$.[10] The final model chosen (isotropic refinement of only one form) is not completely satisfactory, but does permit refinement to convergence and adequately models the main electron density in this region of the unit cell.

The structural results show the C_{12} fragment to be composed of two planar (to ±0.06 Å or $\pm 3\sigma$) portions, one composed of C(40)–C(43) and the other composed of those carbons not bound to rhenium. The dihedral angle between these planes, 43.2°, closely mimics the values found in $(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}$octamethylnaphthalene$)$,[11] 42.4°, and $Ta(\eta^4\text{-}$naphthalene$)(dmpe)_2Cl$,[12] 43.0°. The details of the Re–butadiene bonding are quite conventional, with Re closer to the two central carbons (average Re–C = 2.193 Å) than to the two "end" carbons (average Re–C = 2.346 Å). Also, the three carbon–carbon distances have changed from the short–long–short pattern of both acyclic conjugated dienes and of naphthalene and its derivatives to a long–short–long pattern characteristic of considerable back donation.[13] The remainder of C–C distances in the C_{12} ring are sufficiently flawed by the positional and librational disorder that they do not warrant discussion. Unfortunately, this leaves unanswered the question of whether or not the bond in the five-membered ring (C(50)–C(51)) has been hydrogenated; the bond distance there cannot be used to support bond order 1 or 2.

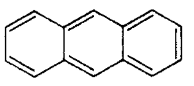
^{1}H NMR. With the X-ray diffraction determination that the $ReH_3(PCy_3)_2$ fragment binds to a butadiene fragment of a C_6 ring, the outstanding question is whether the C_{12} hydrocarbon in II has been hydrogenated (n = 4) or not (n = 2). The most direct answer to this question comes from integration of all hydrogen resonances outside the 2.25–1.27 ppm region assigned to cyclohexyl hydrogens.[14] These integrate to 10 (against each hydride being unit intensity), showing that the C_{12} skeleton has been hydrogenated ($C_{12}H_{10}$). Proposed spectral assignments are detailed in Table IV. Resonances of arene hydrogens 1–3 (remote from the metal) are in the typical aromatic region. Hydrogens 9 and 10, although not equivalent, are assigned to a symmetric multiplet around δ 2.99, a value very near the chemical shift of free acenaphthene (2.98 ppm in C_6D_6). Shifted further and split more asymmetrically (by proximity to the metal) are hydrogens 7 and 8. The coordinated diene resonances are assigned on the basis of observed H–H coupling patterns and the principle that the H(4) chemical shift will differ more from H(5) and H(6) than do these latter from each other.

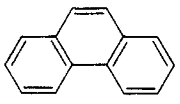
Mechanistic Observations. The product $(\eta^4\text{-}C_{12}H_{10})ReH_3(PCy_3)_2$ is obviously a (hydrogen transfer) rearrangement product of the *adduct* of acenaphthylene with the thermally generated transient $ReH_5(PCy_3)_2$. The fact that the structure adopted is not III may be in part because that structure interrupts the aromatic resonance stabilization within the naphthalene unit. More important, however, is the finding that the coordinated C_{12} hydrocarbon has been hydrogenated at the olefinic bond between the peri carbons. In view of the fact that neither naphthalene (V) nor acenaphthene (VI) show any reaction at 67 °C with $ReH_7(PCy_3)_2$ over 10 half-lives of the acenaphthylene reaction, we judge that the C_{12} hydrocarbon in $(C_{12}H_{10})ReH_3(PCy_3)_2$ is the one which is originally attacked by the transient $ReH_5(PCy_3)_2$; that is, the hydrogenation is wholly intramolecular. Clearly, when the reaction is run with 10-fold excess acenaphthylene and yet none of this $C_{12}H_8$ hydrocarbon is present in the product, coordinated $C_{12}H_{10}$ is inert to substitution by $C_{12}H_8$ in the *final* product. The implication is that the C_{12} fragment initially coordinated is not substituted at any stage of its hydrogenation. Note also that intramolecularity (and hydrogen transfer entirely endo to the metal) is a characteristic of the reaction of the photoproduced transient $ReH_5(PMe_2Ph)_2$ in its reaction with cyclooctatetraene.[15] This stability of hydrogenated, coordinated alkylarene to substitution by external arene is also characteristic of the hydrogenation product of styrene by $IrH_2(Me_2CO)_2(PPh_3)_2^+$.[16]

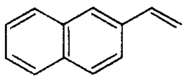

V


VI

It appears that a prerequisite for hydrogenation of a polycyclic aromatic by transient $ReH_5(PCy_3)_2$ is the presence of carbon–carbon unsaturation *not* involved in aromatic resonance structures. Thus, no loss of $ReH_7(PCy_3)_2$ is found after benzene solutions of this hydride are heated (89 °C) with 5 mol of anthracene (VII) for 7 h or with 10 mol of phenanthrene (VIII) for 11 h. The


VII


VIII


IX

[10] Baudry, D.; Ephritikhine, M.; Felkin, H.; Dromzee, Y.; Jeannin, J. *J. Organomet. Chem.* **1984**, *272*, 403.

[11] Hull, J. W.; Gladfelter, W. L. *Organometallics*, **1984**, *3*, 605.

[12] Albright, J. O.; Datta, S.; Dezube, B.; Kouba, J. K.; Marynick, D. S.; Wreford, S. S.; Foxman, B. M. *J. Am. Chem. Soc.* **1979**, *101*, 611.

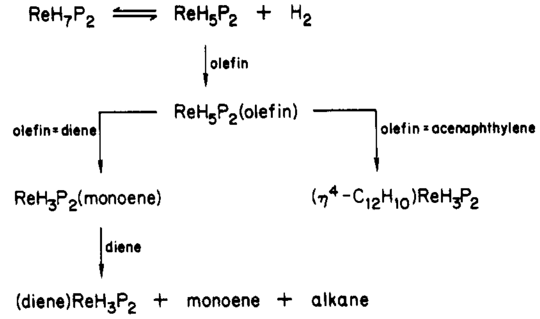
[13] Mingos, D. M. P. In "*Comprehensive Organometallic Chemistry*"; Wilkinson, G., Abel, E., Stone, F., Eds.; Pergamon Press: Oxford, 1982; Vol. 3, p 61.

[14] In $ReH_7(PCy_3)_2$ these hydrogens resonate between 2.22 and 1.20 ppm.

[15] Trimarchi, M. C. L.; Green, M. A.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1985**, *4*, 514.

[16] Crabtree, R. H.; Mellea, M. F.; Quirk, J. M. *J. Am. Chem. Soc.* **1984**, *106*, 2913.

Scheme I



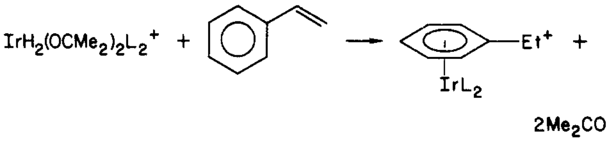
unreactivity toward anthracene also indicates that the rhenium complex is not effective at radical hydrogen transfer, a common mode of hydrogenation at the 9,10-positions of VII.[17] On the other hand, the unreactivity of naphthalene contrasts to the disappearance of $ReH_7(PCy_3)_2$ after being heated (73 °C) in benzene for 3 h in the presence of 10 mol of 2-vinylnaphthalene (IX). The product from 2-vinylnaphthalene displays an AB $^{31}P\{^1H\}$ NMR spectrum which is sharp at −15 °C, broadened at 25 °C, and is a singlet at 72 °C. It thus has characteristics which suggest that it is the 2-ethylnaphthalene analogue of $(\eta^4\text{-}C_{12}H_{10})ReH_3(PCy_3)_2$. 1,3-Cyclohexadiene reacts with $ReH_7(PCy_3)_2$ at 67 °C in cyclohexane at a pseudo-first-order rate constant of 1.2×10^{-2} min^{-1}, quite comparable to the limiting rate constant for $ReH_7(PCy_3)_2$ reacting with acenaphthylene in toluene. This provides a provisional link of common mechanism for $ReH_7(PCy_3)_2$ reacting with arene-conjugated and dienic olefins.

Discussion

An extensive series of $(\eta^4\text{-diene})ReH_3L_2$ complexes have now been characterized.[9,10] Acyclic and nonaromatic cyclic dienes (as well as alkanes) have been employed in their preparation, and the complexes are invariably fluxional. Structures analogous to those now established for $(\eta^4\text{-}C_{12}H_{10})ReH_3(PCy_3)_2$ and for $(\eta^4\text{-}C_6H_8)ReH_3(PPh_3)_2$ were proposed,[9] based on spectral data. The hydride ligands were not detected in either X-ray study, but the P–Re–P angle in $(C_{12}H_{10})ReH_3(PCy_3)_2$, is diagnostic of the presence of *three* hydride ligands in the plane perpendicular to the P–Re–P plane. This angle, 137.3° here and 142.5° in the recently reported $(\eta^4\text{-cyclohexadiene})ReH_3(PPh_3)_2$,[10] is much larger than the 105.6° in $(\eta^5\text{-}C_6H_7)ReH_2(PPh_3)_2$[18] and the 94.5° in $(\eta^5\text{-}C_8H_{11})ReH_2(PMe_2Ph)_2$;[15] the latter two values are smaller because there is no hydride ligand located on the bisector of the P–Re–P angle in the two dihydrides. The Re–PCy_3 distances, 2.42 Å in $(C_{12}H_{10})ReH_3(PCy_3)_2$, are only slightly longer than the 2.38 (1) and 2.41 (1) Å found in $(\eta^4\text{-}C_6H_8)ReH_3(PPh_3)_2$[10] but are still longer than the 2.37 Å found in $(\eta^5\text{-}C_8H_{11})ReH_2(PMe_2Ph)_2$.[15]

It is noteworthy that the reactions of $ReH_7(PPh_3)_2$ with dienes involve *displacement* of hydrogenated diene moiety by external diene[9] (Scheme I), while the aromatic portions of acenaphthylene favor *retention* of the peripherally hydrogenated hydrocarbon. Reactions with these two classes of unsaturated hydrocarbon thus diverge at the stage of the ReH_5L_2(olefin) complex (Scheme I).

The examples of arene capture by rhenium reported here are unusual. We have shown earlier that both $ReH_5(PCy_3)_2$ and $ReH_5(PMe_2Ph)_2$ share the ability to execute H/D exchange with C_6D_6, yet the implied $ReH_5P_2(\eta^2\text{-arene})$ intermediates have never yielded isolable η^4- or η^6-arene complexes.[19] Crabtree has recently reported analogous selectivity in that styrene is hydrogenated and η^6-coordinated by iridium (eq 2). With respect to the ability of



(2)

polyhydride complexes to function as sources of highly reactive "polyunsaturated" species by multiple-hydrogen transfer to an olefin,[20] such "rollover" reactions of Re onto vinylarenes are clearly counterproductive, since arene coordination effectively saturates the desirable 14-electron ReH_3P_2 fragment which we generate in Scheme I. The method thus serves as a general synthesis of ReH_3P_2 bound to a variety of polycyclic aromaics, but the vinylarenes employed are clearly not satisfactory alternatives to *tert*-butylethylene as hydrogen acceptors. On the other hand, this work also shows that arenes lacking pendant vinyl groups are not poisons of unsaturated $ReH_5(PCy_3)_2$ but are unreactive in all but isotope exchange reactions at 70 °C.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society. D.G.D. thanks Augustana College, Rock Island, IL, for support in the form of a sabbatical leave. We thank Cleveland Refractory Metals for material support and Professor R. H. Crabtree for a valuable discussion.

Registry No. I, 208-96-8; $ReH_7(PCy_3)_2$, 92284-90-7; $(\eta^4\text{-}C_{12}H_{10})ReH_3(PCy_3)_2$, 96292-52-3; 2-vinylnaphthalene, 827-54-3; 1,3-cyclohexadiene, 592-57-4.

Supplementary Material Available: Listings of anisotropic *U*'s, distances and angles within the PCy_3 ligand, and observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

---

(17) Feder, H. M.; Halpern, J. *J. Am. Chem. Soc.* **1975**, *97*, 7186.

(18) Baudry, D.; Ephritikhine, M.; Felkin, H.; Jeannin, Y.; Robert, F. *J. Organomet. Chem.* **1981**, *220*, C7.

(19) A η^2-arene complex of the unsaturated fragment $(\eta^5\text{-Cp})ReNO(CO)^+$ has been detected: Sweet, J. R.; Graham, W. A. G. *Organometallics* **1983**, *2*, 135.

(20) Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107.