Synthesis, characterization, and structural study of Re(2,4-C_7H_{11})(H)$_2$(P(C_6H_5)$_3$)$_2$

Thomas E. Waldman [a], Arnold L. Rheingold [*b], and Richard D. Ernst [*a]

[a] *Department of Chemistry, University of Utah, Salt Lake City, UT 84112 (USA)*
[b] *Department of Chemistry, University of Delaware, Newark, DE 19716 (USA)*

(Received June 18th, 1990)

Abstract

Re(2,4-C_7H_{11})(H)$_2$(P(C_6H_5)$_3$)$_2$ has been prepared from the reaction of ReH$_7$(P(C_6H_5)$_3$)$_2$ with 2,4-dimethyl-1,3-pentadiene. A single crystal X-ray diffraction study has revealed a structure with nonequivalent phosphines but equivalent hydride ligands, just the opposite situation as observed for a cyclohexadienyl analog.

Pentadienyl ligands have proven to be very useful in organometallic chemistry [1]. Part of our efforts in this area have been devoted to gaining an understanding of how these ligands compare to the more familiar cyclopentadienyl system. One notable difference between these ligands seems to be that higher oxidation state metal-pentadienyl compounds are not common, and perhaps not generally stable [2]. To date, there are even few such compounds involving metals in the trivalent oxidation state [3], although some related cyclohexadienyl, etc. species have been reported [4]. However, while one would expect cyclohexadienyl ligands to be most closely related to pentadienyl ligands, there is some evidence that suggests the former ligands to be actually intermediate between cyclopentadienyl and pentadienyl ligands in their behavior [5]. Hence, one may expect to see significant differences between pentadienyl and cyclohexadienyl ligands. One interesting cyclohexadienyl complex which attracted our attention is Re(C_6H_7)(H)$_2$-(P(C_6H_5)$_3$)$_2$, which is unusual for the formal metal oxidation state as well as the presence of two hydride ligands [6]. We have therefore sought to prepare an open pentadienyl analog, and report herein our observations for Re(2,4-C_7H_{11})(H)$_2$(P-(C_6H_5)$_3$)$_2$ (C_7H_{11} = dimethylpentadienyl).

Experimental

All operations involving organometallic compounds were carried out under prepurified nitrogen in Schlenk apparatus or in a glovebox. Acetone and methylene chloride were dried by distillation under MgSO$_4$ and P$_4$O$_{10}$, respectively. Other solvents were dried and degassed by distillation from benzophenone ketyl under

nitrogen. Spectroscopic data were recorded as previously described [7]. Elemental analyses were obtained from Desert Analytics.

Re(2,4-C$_7$H$_{11}$)(H)$_2$(P(C$_6$H$_5$)$_3$)$_2$. A 100 mL 3-neck flask equipped with a reflux condenser, magnetic stirring bar, and nitrogen inlet was charged with 1.00 grams (1.39 mmol) of ReH$_7$(P(C$_6$H$_5$)$_3$)$_2$ [8]. Approximately 10 mL of THF, 1.65 mL (13.9 mmol) of 2,4-dimethyl-1,3-pentadiene, and 1.8 mL (13.9 mmol) of 3,3-dimethyl-1-butene were added by syringe. A rapid color change from pale yellow to orange was noted upon addition of the 3,3-dimethyl-1-butene. The reaction mixture was brought to a gentle reflux for ca. 10 minutes, during which time the color darkened steadily to a deep red. Removal of the solvent in vacuo resulted in a reddish colored foam that was extracted with four 30 mL portions of acetone. The acetone extracts were filtered through a 1 inch pad of Celite on a coarse frit, resulting in a bright yellow filtrate and a small amount of red solid left on the Celite pad. The frit was attached to a clean flask and extraction with 40 mL of CH$_2$Cl$_2$ resulted in a clear red filtrate. The bright yellow acetone extracts were concentrated in vacuo to ca. 100 mL and cooled to $-20\,^\circ$C overnight. The resulting air-stable yellow crystals were isolated after removal of the supernatant, yielding 0.62 g (55%) of product. The bright red coproduct was identified (melting point, NMR spectroscopy) as Re$_2$H$_8$(P(C$_6$H$_5$)$_3$)$_4$ (0.38 g, 38%) [9].

Anal. Found: C, 63.27; H, 5.34. C$_{43}$H$_{43}$ReP$_2$ calcd.: C, 63.92; H, 5.36%. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.4 (m, 30H), 5.1 (s, 1H), 2.58 (s, 2H), 1.63 (s, 6H), -0.8 (s, 2H), -7.8 (t, 2H, J(PH) 41.5 Hz—at $-40\,^\circ$C the couplings were nonequivalent at 35 and 48 Hz). ^{13}C NMR (CD$_2$Cl$_2$): δ 133.9 (6C, dd, J(CP) 10.6 Hz, J(CH) 164 Hz), 128.5 (12C, dd, J(CP) 9.3 Hz, J(CH) 161 Hz), 127.3 (12C, dd, J(CP) 9.6 Hz, J(CH) 159 Hz), 103.9 (1C, d, J(CH) 164 Hz), 97.8 (2C, s), 45.22 (2C, t, J(CH) 149 Hz), 28.1 (2C, q, J(CH) 125 Hz). ^{31}P NMR (CD$_2$Cl$_2$): δ 39 (2P, br s). $-40\,^\circ$C: δ 41.45 (1P,

Table 1

Crystallographic data for Re(2,4-C$_7$H$_{11}$)(H)$_2$(PPh$_3$)$_2$

(a) Crystal parameters			
formula	C$_{43}$H$_{43}$P$_2$Re	β, deg	96.68(1)
formula weight	807.92	V, Å^3	3588(1)
crystal system	monoclinic	Z	4
space group	$P2_1/n$	μ(Mo-K_α), cm^{-1}	37.0
a, Å	14.001(2)	T, K	295
b, Å	15.663(3)	color	yellow green
c, Å	16.472(3)	size, mm	0.24 × 0.30 × 0.30
(b) Data collection			
diffractometer	Nicolet $R3m/\mu$	observed reflections	4173 ($3\sigma F_o$)
radiation	Mo-K_α	R(merge)	0.020
wavelength, Å	0.71073	T_{max}/T_{min}	1.380
scan range, deg	$4 \le 2\theta \le 48$	standard reflections	3 standards/197 reflections
reflections collected	6080	variation in standards, %	<1
independent reflections	5620		
(c) Refinement			
$R(F)$	0.0335	N_o/N_v	11.25
$R(wF)$	0.0379	$\Delta\sigma$(final)	0.01
GOF	1.032	$\Delta(\rho)$, e Å^{-3}	0.68

br d, J(PP) 22 Hz), 36.89 (1P, br d, J(PP) 22 Hz). Coalescence temperature, 40 °C (121.4 MHz).

X-ray diffraction study of Re(2,4-C_7H_{11})(H)$_2$(P(C_6H_5)$_3$)$_2$. Single crystals of this

Table 2

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{Å}^2 \times 10^3$) for Re(2,4-C_7H_{11})(H)$_2$(PPh$_3$)$_2$

Atom	x	y	z	U^a
Re	2717.8(2)	1703.2(2)	465.2(2)	26(1)
P(1)	1220(1)	1932(1)	940(1)	25(1)
P(2)	3069(1)	2838(1)	−356(1)	28(1)
C(1)	3293(5)	1179(4)	1697(4)	40(2)
C(2)	4101(5)	1261(4)	1227(4)	40(2)
C(3)	4098(5)	922(4)	431(5)	39(2)
C(4)	3324(5)	503(4)	−36(4)	40(2)
C(5)	2459(6)	286(4)	289(6)	47(3)
C(6)	4937(5)	1832(5)	1558(5)	52(3)
C(7)	3435(6)	304(5)	−918(5)	60(3)
C(11)	1858(2)	3117(3)	2167(3)	35(2)
C(12)	1738	3716	2774	45(3)
C(13)	818	3998	2889	48(3)
C(14)	19	3682	2396	45(3)
C(15)	139	3083	1789	37(2)
C(16)	1059	2801	1675	29(2)
C(21)	913(3)	1058(2)	2398(2)	42(3)
C(22)	660	355	2846	57(3)
C(23)	340	−394	2444	56(3)
C(24)	273	−440	1594	52(3)
C(25)	526	264	1145	37(2)
C(26)	846	1013	1547	29(2)
C(31)	−748(3)	1742(3)	236(2)	39(2)
C(32)	−1523	1943	−343	45(3)
C(33)	−1395	2501	−982	46(3)
C(34)	−492	2857	−1041	45(3)
C(35)	282	2655	−462	37(2)
C(36)	154	2097	177	27(2)
C(41)	2387(4)	4196(3)	538(3)	52(3)
C(42)	1822	4911	648	70(4)
C(43)	1288	5293	−23	77(4)
C(44)	1317	4958	−804	77(4)
C(45)	1882	4243	−915	57(3)
C(46)	2416	3862	−244	35(2)
C(51)	4689(3)	3841(3)	279(3)	43(3)
C(52)	5671	4022	397	58(3)
C(53)	6313	3524	15	61(3)
C(54)	5974	2843	−484	55(3)
C(55)	4992	2662	−602	42(3)
C(56)	4350	3161	−220	34(2)
C(61)	2305(3)	2130(3)	−1884(3)	50(3)
C(62)	2146	2113	−2735	60(3)
C(63)	2593	2713	−3191	70(4)
C(64)	3199	3328	−2795	65(3)
C(65)	3359	3344	−1944	55(3)
C(66)	2911	2745	−1488	34(2)

^{a} Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 3

Selected bond distances (Å) and angles (°) for Re(2,4-C$_7$H$_{11}$)(H)$_2$(PPh$_3$)$_2$

Re–P(1)	2.350(2)	Re–Hre(1)	1.58(5)
Re–P(2)	2.320(2)	Re–Hre(2)	1.70(5)
Re–C(1)	2.249(7)	C(1)–C(2)	1.449(10)
Re–C(2)	2.289(6)	C(2)–C(3)	1.413(10)
Re–C(3)	2.293(7)	C(3)–C(4)	1.416(9)
Re–C(4)	2.258(7)	C(4)–C(5)	1.421(12)
Re–C(5)	2.262(7)		
P(1)–Re–P(2)	109.6(1)	Hre(1)–Re–Hre(2)	131(2)
P(1)–Re–Hre(1)	77(2)	C(1)–C(2)–C(3)	123.0(6)
P(1)–Re–Hre(2)	84(2)	C(2)–C(3)–C(4)	126.7(7)
P(2)–Re–Hre(1)	76(2)	C(3)–C(4)–C(5)	122.5(7)
P(2)–Re–Hre(2)	69(2)		

compound were obtained by very slow partial evaporation of a solution in a mixture of CH$_2$Cl$_2$ and THF. This was carried out in a closed vessel having two chambers, one for the solution, the other for toluene, so that predominantly CH$_2$Cl$_2$ vapors would be transferred to the toluene [10].

Crystallographic data are summarized in Table 1. The space group was uniquely defined by systematic absences. Data were collected using omega scans, and corrected empirically for absorption. The SHELXTL (5.1) program package was utilized for all calculations (G. Sheldrick, Nicolet XRD, Madison, WI). The rhenium atom position was located by heavy atom methods. Subsequent difference Fourier syntheses revealed the remaining non-hydrogen atom locations as well as the hydrogen atoms bonded to C(1), C(3), and C(5). The non-hydrogen atoms were refined anisotropically, while the aforementioned hydrogen atoms were treated isotropically. Other hydrogen atoms were placed in idealized locations. The phenyl rings were treated as rigid, planar hexagons. Atomic coordinates are given in Table 2, and selected bond distances and angles are provided in Table 3. Additional bonding, thermal, and structure factors may be obtained from the authors.

Results and discussion

The reaction of ReH$_7$(P(C$_6$H$_5$)$_3$)$_2$ with benzene and 3,3-dimethylbutene has been reported to yield Re(C$_6$H$_7$)(H)$_2$(P(C$_6$H$_5$)$_3$)$_2$ [6], and we have now found that by substituting 2,4-dimethyl-1,3-pentadiene for the benzene, the analogous, completely open pentadienyl compound, Re(2,4-C$_7$H$_{11}$)(H)$_2$(P(C$_6$H$_5$)$_3$)$_2$, may also be isolated. In this case, however, a hydrogen atom is abstracted from, rather than added to, the organic substrate. The presence of the added olefin seems crucial to the reaction [11], as without it we could not isolate significant amounts of the product. Furthermore, the utilization of other diene molecules which do not favor the U conformation (e.g., 2,3-dimethyl-1,3-pentadiene) appeared to lead to diene rather than dienyl complexes.

Notably, while the ^{1}H NMR spectra of the cyclohexadienyl (and a subsequently reported cyclooctadienyl [12]) complex reveal two nonequivalent hydride ligands, the spectrum for the 2,4-C$_7$H$_{11}$ complex indicates that its hydride ligands are
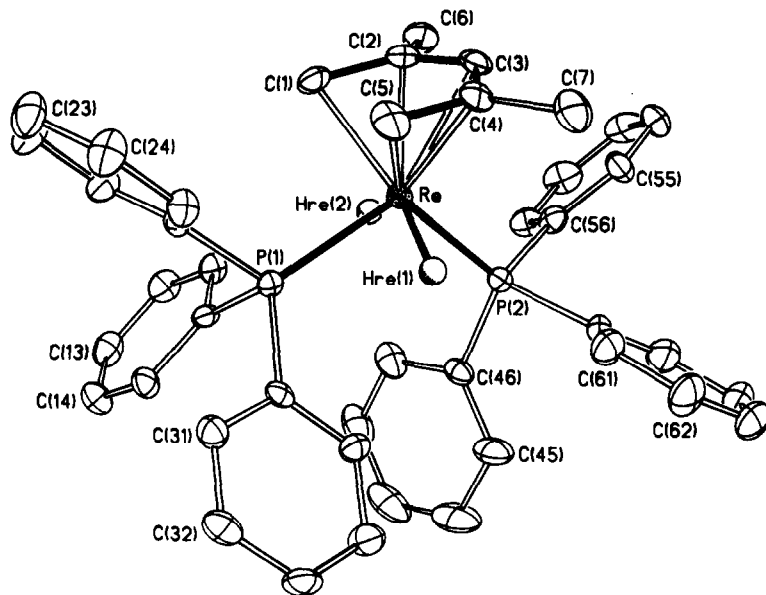
Fig. 1. Perspective view and numbering scheme for $Re(2,4-C_7H_{11})(H)_2(P(C_6H_5)_3)_2$.

equivalent, whereas the phosphine ligands are nonequivalent. These data would suggest structures I and II respectively, for these compounds, and are in accord with structural results for each (vide infra). In the case of $Re(2,4-C_7H_{11})(H)_2(P(C_6H_5)_3)_2$, higher temperature ^{31}P NMR spectra do display a single phosphine resonance, and from the coalescence temperature of $40\,^\circ C$, one can calculate a barrier to the pentadienyl ligand oscillation (ΔG^*) of 13.9 (2) kcal/mol [13].
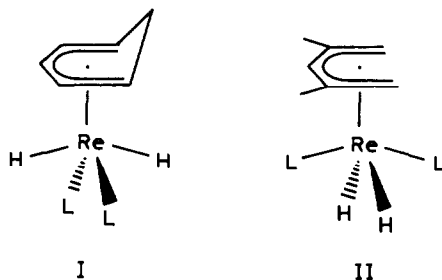
The solid state structure of $Re(2,4-C_7H_{11})(H)_2(P(C_6H_5)_3)_2$ may be seen in Fig. 1, while pertinent bonding parameters are contained in Tables 2 and 3. The structure does indeed correspond to II, and quite fortunately both hydride ligands could be located and refined. Their observed positions, 1.58(5) and 1.70(5) Å from the rhenium center, and 2.99(5) Å apart, confirm the formulation of this compound as a Re(III) dihydride, rather than that of a Re(I) complex of H_2, as could be considered based on the general preference for pentadienyl ligands to bind to metals in lower oxidation states. The five metal-bound carbon atoms of the pentadienyl ligand are nearly planar, the maximum deviation from the plane being 0.037 Å, while larger deviations are found for the methyl substituents, 0.187 and 0.200 Å,
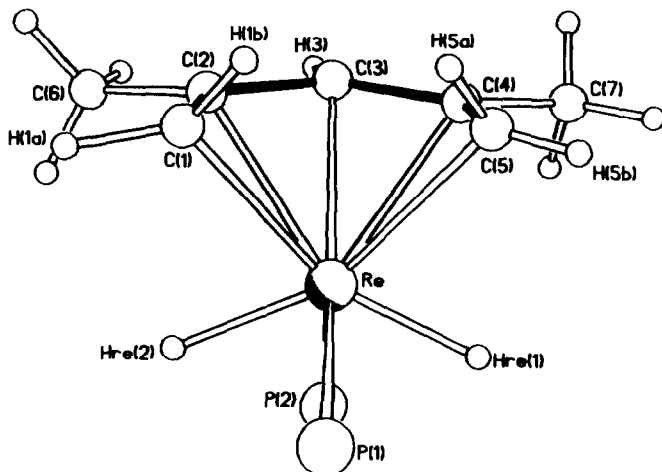
Fig. 2. Alternate view of the molecule, emphasizing the inner coordination sphere and the dienyl hydrogen atoms.

corresponding to tilts of 7.1 and 7.6°, respectively [14*]. Similar deviations (tilts) toward the metal atom are observed for H(1a) (0.17 Å, 9.4°), H(3) (0.06 Å, 3.3°), and H(5b) (0.07 Å, 4.2°), whereas the opposite is observed for H(1b) (−0.71 Å, −42.0°) and H(5a) (−0.69 Å, −44.2°), as expected [1a,2]. The deviations of P(1) and P(2) from this plane differ significantly at 2.432 and 3.487 Å, corresponding to respective tilts of 18.9 and 51.5° beneath the rhenium atom position [15*]. The significant upward tilt of P(1) relative to P(2) is reasonable, and may be ascribed to an attempt of the ligand to position itself in a region of relatively unused metal orbital density [16]. For comparison, the tilts of the hydride ligands are 2.30 and 2.38 Å (113 and 115°), respectively. The rhenium atom is situated 1.671 Å from the ligand plane.

The average Re–C bond distance of 2.270(7) Å is indistinguishable from the values of 2.28(2) Å in $Re(C_6H_7)(H)_2(P(C_6H_5)_3)_2$ or 2.245(5) Å in $Re(C_8H_{11})(H)_2(P(CH_3)(C_6H_5)_2)$. A slight preference by rhenium for the carbon atoms at the open end of the pentadienyl ligand seems to exist, as the Re–C(3) and average Re–C(2,4) and Re–C(1,5) distances are 2.293(7), 2.274(5), and 2.256(5) Å, respectively. Interestingly, the Re–P(1) bond is longer than the Re–P(2) bond, 2.350(2) vs. 2.320(2) Å, respectively [17*], but both bonds are shorter than the average distances of 2.355(5) and 2.366(2) Å reported for the cyclohexadienyl and cyclooctadienyl analogs. The P(1)–Re–P(2) angle of 109.6(1)° compares well with the value of 105.6(2)° in the cyclohexadienyl analog, despite the difference in orientation. The H–Re–H angle of 131(3)° is noticeably larger, but similar to the value of 125(6)° in the cyclooctadienyl analog.

Acknowledgement

---

* Reference number with asterisk indicates a note in the list of references.

References

1 (a) R.D. Ernst, Acc. Chem. Res., 18 (1985) 56; (b) H. Yasuda and A. Nakamura, J. Organomet. Chem., 15 (1985) 285; (c) P. Powell in R. West and F.G.A. Stone, (Eds.), Advances in Organometallic Chemistry, Academic, New York, 1986; Vol. 26, p. 125; (d) C.G. Kreiter, ibid., p. 297.

2 R.D. Ernst, Chem. Rev., 88 (1988) 1255.

3 (a) R.D. Ernst, H. Ma, G. Sergeson, T. Zahn, and M.L. Ziegler, Organometallics, 6 (1987) 848; (b) E. Melendez, A.M. Arif, A.L. Rheingold, and R.D. Ernst, J. Am. Chem. Soc., 110 (1988) 8703.

4 (a) P.T. Draggett, M. Green, and S.F.W. Lowrie, J. Organomet. Chem., 135 (1977) C60; (b) R.H. Crabtree and R.P. Dion, J. Chem. Soc., Chem. Commun., (1984) 1260; (c) N.A. Bailey, E.H. Blunt, G. Fairhurst, and C. White, J. Chem. Soc., Dalton Trans., (1980) 829.

5 P.T. DiMauro and P.T. Wolczanski, Organometallics, 6 (1987) 1947.

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

7 L. Stahl and R.D. Ernst, J. Am. Chem. Soc., 109 (1987) 5673.

8 J.D. Allison, T.E. Wood, R.E. Wild, and R.A. Walton, Inorg. Chem., 21 (1982) 3540.

9 (a) J. Chatt and R.S. Coffey, J. Chem. Soc. A, (1969) 1963; (b) R. Bau, W.E. Carroll, R.G. Teller, and T.F. Koetzle, J. Am. Chem. Soc., 99 (1977) 3872.

10 R.J. Neustadt, T.H. Cymbaluk, R.D. Ernst, and F.W. Cagle, Jr., Inorg. Chem., 19 (1980) 2375.

11 R.H. Crabtree and C.P. Parnell, Organometallics, 4 (1985) 519.

12 M.C.L. Trimarchi, M.A. Green, J.C. Huffman, and K.G. Caulton, Organometallics, 4 (1985) 519.

13 (a) This value results from $T_c = 313.15$ K and $\Delta\nu = 546.6$ Hz [13b]; (b) H. Kessler, Angew. Chem. Int. Ed. Engl., 9 (1970) 219.

14 For a given substituent attached to a pentadienyl atom X, the sine of the tilt angle θ is defined as the displacement of a given atom from the least squares plane divided by the distance between this atom and atom X.

15 The sine of the tilt angle is defined as the distance of the substituent below the rhenium atom position divided by the Re-substituent distance.

16 (a) H. Ma, P. Weber, M.L. Ziegler, and R.D. Ernst, Organometallics, 6 (1987) 854; (b) T.D. Newbound, J.W. Freeman, D.R. Wilson, M.S. Kralik, A.T. Patton, C.F. Campana, and R.D. Ernst, ibid., 6 (1987) 2432.

17 The longer Re-P(1) bond could be a result of the fact that P(1) but not P(2) resides nearly opposite to a metal-bound carbon atom (a *trans* influence), or to the fact that the site by the open pentadienyl edge actually seems to encounter significant steric crowding [18].

18 T.D. Newbound, L. Stahl, M.L. Ziegler, and R.D. Ernst, Organometallics, in press.