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The Molecular Structure of (1,5-Hexadiene)(maleic anhydride)Pt(0)

G. BENNETT STACKHOUSE, IV and LAURA L. WRIGHT*

Department of Chemistry, Furman University, Greenville, S.C. 29613, U.S.A.

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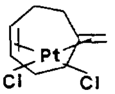
The extent of π back bonding in metal olefin complexes has been studied extensively for d^8 transition metal complexes. In order to optimize the bonding in square planar olefin complexes of Pd(II) and Pt(II) it has been observed that the olefin binds in an upright perpendicular orientation with respect to the coordination plane as found in Zeise's salt [1]. Recent studies have shown that the preference for this coordination geometry is due in large part to steric interactions between the olefin and its *cis* neighbors. Rettig and coworkers [2] have shown that Pt(II) complexes can be synthesized which have an olefin bound in the in-plane orientation, **1**.



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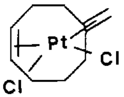

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In these examples, coordination of one double bond in the normal upright configuration causes the other double bonds to coordinate in the unusual in-plane configuration. The net result is that the exocyclic carbon atom comes into very close contact with the neighboring *cis* chloro ligand producing a substantial steric repulsion. These studies have shown that in four-coordinate square planar complexes it is electronically possible to coordinate alkenes in either the upright perpendicular or the in-plane orientation while still allowing π back bonding to occur. The observed coordination preference in these d^8 systems stems from steric interactions rather than orbital constraints.

If trigonal planar Pt(0) olefin complexes are next considered an immediate difference is observed in the preferred coordination orientation of the olefin. In almost all known olefin complexes of three coordinate Pt(0), the alkenes are coordinated with the in-plane orientation [3]. Rösch and Hoffman [4] have used the Extended Hückel Molecular Orbital method to calculate that the amount of back bonding is optimized in olefin complexes of the type tris(ethylene)Ni(0) when all three double bonds are coplanar. Their calculations indicated that if the three ethylenes rotated into the upright perpendicular orientation, the total energy of the molecule would increase and the π back bonding between the metal and the ethylenes would diminish.

It was of interest to our group to evaluate the extent of the loss in back bonding when an olefin coordinates to a Pt(0) atom in an out-of-plane orientation. In order to do this we initiated a study of Pt(0) diene complexes. At this time we would like to report the molecular structure of one of these complexes which provides an interesting example of what happens when an alkene coordinates to Pt(0) in an out-of-plane orientation.

Experimental

The (1,5-hexadiene)(maleic anhydride)Pt(0) complex was synthesized from tris(tribenzylideneacetylacetone)triplatinum(0), 1,5-hexadiene and maleic anhydride as reported previously [5]. To an acetone solution of 150 μl (1.27 mmol) of 1,5-hexadiene and 0.050 g (0.51 mmol) of maleic anhydride is added 0.10 g (0.056 mmol) of tris(tribenzylideneacetylacetone)triplatinum(0)·$CHCl_3$ under a N_2 atmosphere. After *ca.* 24 h the resulting yellow solution is filtered, evaporated, and extracted with diethyl ether to leave behind as a white solid the product, (1,5-hexadiene)(maleic anhydride)Pt(0). Crystals suitable for a single crystal X-ray diffraction study were obtained by slow evaporation of a diethyl ether/acetone solution. Crystal data is summarized in Table I.

TABLE I. Crystallographic Data

Empirical formula	$C_{10}H_{12}O_3Pt$
Formula weight	375.2 daltons
Space group	$P_{na}21$
Z	4
a (Å)	16.375(3)
b (Å)	4.989(2)
c (Å)	12.225(2)
V (Å^3)	999
D_x (g/cm^3)	2.47
λ(Mo Kα) (Å)	0.71073
μ(Mo Kα) (cm^{-1})	141.6
Crystal size	0.32 × 0.19 × 0.09 mm
Temperature (°C)	25

Data Collection and Processing

A CAD4 diffractometer in the $\theta/2\theta$ mode with variable scan speed and graphite-monochromated

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*Author to whom correspondence should be addressed.

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Mo Kα radiation was used to measure 1897 reflections with $3.0° \leqslant 2\theta \leqslant 50°$. Of these, there were 880 unique reflections among which 790 had $F > 3\sigma(F)$. Analytical absorption corrections were applied (min = 9.9, max = 31.5, average = 24.2) as was a linear decay correction (a 1.9% decay over 55 h exposure time as indicated by three standard reflections monitored every 2.5 h).

Structure Analysis and Refinement

The heavy atom method was used employing the SHELX76 structure determination package [6]. The Pt was located from a Patterson map, and subsequent non-hydrogen atoms were located from difference Fourier maps. Hydrogen atoms were not located. Full-matrix least-squares refinement was performed with all non-hydrogen atoms anisotropic. The weighting scheme used was $w = 1/[\sigma^2(F_o) + 0.0004F_o^2]$. Final R and R_w values are 0.046 and 0.056. The largest peak in the final difference Fourier map had an intensity of 1.7 e/Å^3 at a distance of 0.8 Å from the Pt atom. Selected bond distances and angles are listed in Table II and Table III, respectively.

TABLE II. Interatomic Distances (Å)[a]

Pt–C2	2.24(3)	O3–C4	1.23(3)
Pt–C3	2.07(2)	C1–C2	1.48(3)
Pt–C5	2.15(2)	C2–C3	1.40(3)
Pt–C6	2.25(2)	C3–C4	1.51(3)
Pt–C9	2.30(2)	C5–C6	1.30(3)
Pt–C10	2.32(2)	C6–C7	1.51(3)
O1–C1	1.41(3)	C7–C8	1.55(3)
O1–C4	1.34(3)	C8–C9	1.53(3)
O2–C1	1.21(3)	C9–C10	1.28(3)

[a] e.s.d.s given in parentheses.

TABLE III. Selected Bond Angles (°)[a]

C2–Pt–C3	37.5(9)	C1–C2–C3	108(2)
C2–Pt–C5	95.1(9)	C2–C3–C4	104(2)
C5–Pt–C6	34.2(9)	O1–C4–O3	123(2)
C6–Pt–C9	76.6(8)	O1–C4–C3	111(2)
C9–Pt–C10	32.1(8)	O3–C4–C3	126(2)
C3–Pt–C10	90.4(7)	C5–C6–C7	137(2)
C1–O1–C4	108(2)	C6–C7–C8	105(2)
O1–C1–O2	115(2)	C7–C8–C9	102(2)
O1–C1–C2	108(2)	C8–C9–C10	130(2)
O2–C1–C2	137(2)		

[a] e.s.d.s given in parentheses.

Results and Discussion

Figure 1 shows the molecular structure which was determined for (1,5-hexadiene)(maleic anhydride)Pt(0). As can be seen, the maleic anhydride double bond (C2=C3) and one of the hexadiene double bonds (C5=C6) are bonded in the trigonal coordination plane of the platinum atom as expected for a three coordinate Pt(0) species. The second

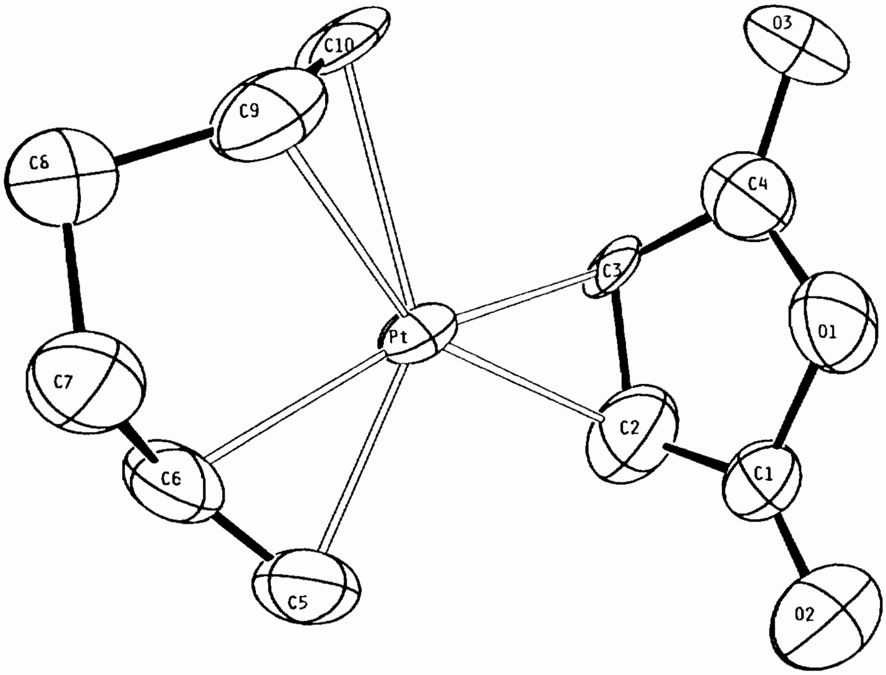
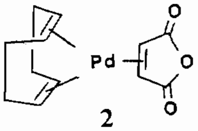


Fig. 1. Perspective drawing of (1,5-hexadiene)(maleic anhydride)Pt(0), thermal ellipsoids are drawn at 50% probability level.

hexadiene double bond (C9=C10) however, is rotated 27° out of the coordination plane. An analysis of the bond distances observed in this complex is informative. The electron deficient olefin, the maleic anhydride, is bound the closest to the metal center with the distance between the metal atom and the midpoint of the double bond (C2=C3) being 1.96(3) Å. This is consistent with the idea that the π back bonding from the full d orbital of the metal to the empty π^* orbital of the olefin increases as the energy match between the d orbital and the π^* orbital improves [3a, 7]. The diene is bonded unsymmetrically with the out-of-plane double bond being the farthest from the metal center with the Pt to midpoint of the C9=C10 distance being 2.22(2) Å and the in-plane double bond being at an intermediate distance with the Pt to midpoint of the C5=C6 distance being 2.05(2) Å. This 0.17 Å difference in the metal olefin distances is a clear indicator that the metal–olefin bonding interaction has diminished substantially. The 27° rotation out-of-plane for the C9=C10 double bond results in a diminished overlap between the π^* orbital and a full metal orbital as required for participation in π back bonding.

The question remaining is whether a full 90° rotation into the upright orientation would reestablish the π back bonding. It was with interest that we noted the report by Itoh of the structure of a related Pd(0) complex, (1,5-cyclooctadiene)(maleic anhydride)Pd(0) (2) [8]. In this molecule the double bonds of the 1,5-cyclooctadiene are forced to coordinate in the upright orientation due to the cyclic nature of the ligand. Again, the maleic anhydride is bonded very close to the metal with the Pd to midpoint distance being 1.93(2) Å. A comparison of the upright cyclooctadiene double bonds shows a lengthening of the Pd–midpoint distances to 2.15(2) Å each.



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Since the radii of Pd and Pt atoms are nearly identical it is now possible to compare the range of various bonding orientations to obtain a qualitative ordering for the extent of π back donation. As indicated in Table IV, in both of these molecules the maleic anhydride is coordinated in the in-plane orientation and is found at the shortest distance from the metal atom, 1.96(3) Å in the platinum complex and 1.92(2) Å in the palladium complex. The in-plane coordination is the predicted most favorable one, and the electron deficient nature of this alkene allows for better orbital overlap for the π back donation. The in-plane C5=C6 double bond in 1,5-hexadiene is the next shortest in this series with the Pt–midpoint distance of 2.05(2) Å. The 0.09 Å lengthening of this metal–alkene interaction is due to the change in the electronic nature of the alkene. The orbital energy match for the π back donation is now not quite as good as in the maleic anhydride, but the orientation of the coordinated alkene is still favorable.

TABLE IV. Coordination Geometry and Bond Distances Comparisons

Double bond	Angle out of coordination plane (°)	Metal to midpoint distance (Å)
(1,5-Cyclooctadiene)(maleic anhydride)Pd(0) [8]		
Maleic anhydride	0	1.93(2)
1,5-Cyclooctadiene	90	2.15(2)
(1,5-Hexadiene)(maleic anhydride)Pt(0)		
Maleic anhydride	0	1.96(3)
C5–C6	0	2.05(2)
C9–C10	27	2.22(2)

If a comparison is now made between the C5=C6 double bond of 1,5-hexadiene, the C9=C10 double bond of 1,5-hexadiene, and the 1,5-cyclooctadiene double bonds some interesting observations can be made. These latter double bonds are both oriented out of the coordination plane but possess the same electronic nature as the in-plane C5=C6 double bond in the 1,5-hexadiene. Since the electronic properties are now similar, the differences in bond distances can be attributed to changes in the π back bonding resulting from changes in coordination orientation. The in-plane C5=C6 bond is the closest to a metal, 2.05(2) Å, the perpendicular upright cyclooctadiene double bonds are next, 2.15(2) Å, and the skewed C9=C10 bond is the farthest from a metal, 2.22(2) Å. While the difference is not very large for the latter two cases the orientation which appears to be the least stable is the one which places the alkene in an orientation where there are no d orbitals available for back bonding. Both the in-plane and the upright alkenes are closer to the metal than the C9=C10 bond at its angle of 27°. Thus even in the disfavored upright orientation there is apparently some π back donation occurring. Thus the overall trend for π back donation in these two related three coordinate d^{10} metal complexes is in-plane, electron deficient > in-plane, electron rich > upright, electron rich > skewed (orientation angle $\neq 0° \neq 90°$), electron rich.

Supplementary Material

Final atomic coordinates and thermal parameters, bond lengths and angles, and structure factors (F_o/F_c) are available from author L. L. Wright on request.

Acknowledgements

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