Journal of Organometallic Chemistry, 59 (1973) 395–401

INFRARED AND NUCLEAR MAGNETIC RESONANCE STUDIES OF PALLADIUM(0)–MALEIC ANHYDRIDE COMPLEXES

H. MINEMATSU, Y. NONAKA, S. TAKAHASHI and N. HAGIHARA
The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565 (Japan)
(Received January 30th, 1973)

SUMMARY

In the complexes, L_2Pd(maleic anhydride) [L = $(p\text{-}CH_3OC_6H_4)_3P$, $CH_3(C_6H_5)_2P$, $(p\text{-}ClC_6H_4)_3P$, $(C_6H_5O)_3P$, $CH_3C(CH_2O)_3P$, $(C_6H_5)_3P$], the chemical shifts and the carbonyl stretching frequencies of the maleic anhydride ligand are linearly related to the basicities of the phosphorous ligands (L). As the basicity of L increases, ν(CO) moves to lower wavenumbers, whereas the signal for the maleic anhydride protons unexpectedly shifts downfield.

INTRODUCTION

In recent years a great many metal–olefin complexes have been prepared and the nature of their bonding has been discussed on the basis of spectroscopic observations. Orchin *et al.*[1], in a systematic study of divalent platinum–ethylene complexes, found that the chemical shifts of olefinic protons in a series of *trans*-$PtCl_2$-(*para*-substituted pyridine *N*-oxide)(C_2H_4) complexes moved downfield as the electron-withdrawing character of the *para*-substituent increased, a fact ascribed to a reduction in π back-donation from the metal to ethylene.

On the other hand, there seem to have been no systematic IR and NMR investigations of the zerovalent olefin complexes. Previously we reported[2] the preparation and the spectroscopic characteristics of the complexes $[(C_6H_5)_3P]_2M$(Un) (M = Pd, Pt; Un = activated olefins and quinones), which serve as efficient catalysts for the dimerization of butadiene[3].

In this paper we describe the effect of various phosphorus ligands on the chemical shift and the carbonyl stretching frequency of the maleic anhydride ligand in L_2Pd(maleic anhydride).

RESULTS AND DISCUSSION

PMR spectrum of $[(C_6H_5)_3P]_2Pd$*(maleic anhydride)*

We previously reported[2] that the 60 MHz NMR spectra (in benzene-d_6) of olefinic protons in both bis(triphenylphosphine)palladium maleic anhydride and dimethylfumarate complexes showed an AB coupling pattern. This was, at that time, interpreted in terms of olefins bound unsymmetrically to palladium. It has, however,

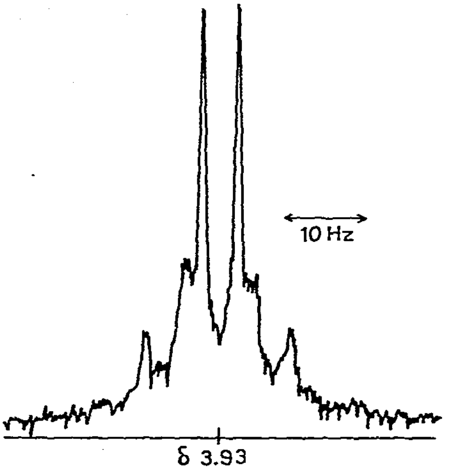

Fig. 1. 100 MHz PMR spectrum of olefinic protons in $[(C_6H_5)_3P]_2Pd$(maleic anhydride) in benzene-d_6 solution at 25°.

become clear by comparison with the 100 MHz spectrum (Fig. 1) of the maleic anhydride complex in benzene-d_6 solution that an apparent AB type pattern is not responsible for the non-identity of the two olefinic protons, but for the second order coupling of protons with the *cis* and *trans* phosphorous ^{31}P atoms. If we postulate a planar maleic anhydride complex (Fig. 2), it is readily understandable that four different coupling constants, *i.e.*, $J(P^1–P^2)$, $J(H^1–H^2)$, $J(P^1–H^1)=J(P^2–H^2)$, and $J(P^2–H^1)=J(P^1–H^2)$ would exist. This is a typical AA'XX' system, in which hydrogen atoms H^1, H^2 are no longer magnetically equivalent. Consequently, the spectrum of

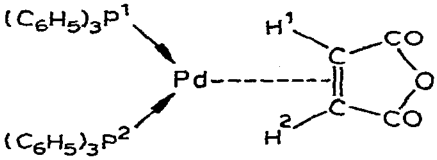

Fig. 2.

maleic anhydride protons centered at δ 3.93 ppm (Fig. 1) can be analyzed as part of an AA'XX' multiplet which should consist theoretically of ten lines, symmetrically disposed about the mid point[4]. Owing to the difficulty in detecting all ten lines, we could not calculate values for *cis* and *trans* coupling constants, however the sum, $J(P–H)_{cis}+J(P–H)_{trans}$, which can readily be obtained from the spacing of the two most intense lines, is 4.4 Hz*.

Complexes of this type have been found, by X-ray methods[5–9], to have approximately planar configurations in the solid state. Recent molecular orbital calculations[10] have shown this configuration to be energetically more stable than the tetrahedral. The observation of an AA'XX' pattern here would imply the same structure in the solid state.

---

* The corresponding value for the complex $[(C_6H_5)_3P]_2Pd$(dimethyl fumarate) is 5.4 Hz.

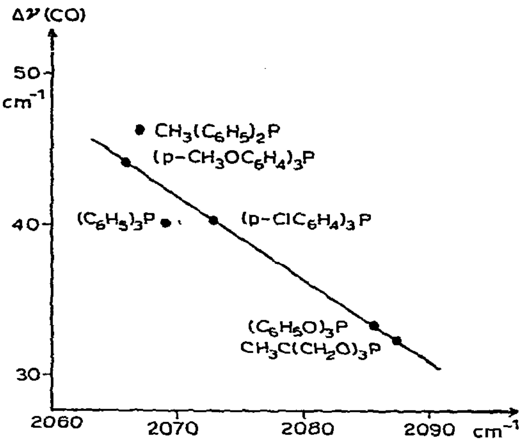

Fig. 3. Correlation between $\Delta\nu$(CO) of maleic anhydride in L_2Pd(maleic anhydride) and ν(CO) (A_1) of Ni(CO)$_3$L. The $\nu_1 f-\nu_1$ only is plotted; the $\nu_2 f-\nu_1$ also shows a similar correlation.

Although the NMR spectra were recorded in the temperature range 30–70°, the resonance pattern showed no temperature dependence, which suggests that maleic anhydride is rigidly bound to palladium and that there is no rotation about the metal ligand axis. When an equimolar quantity of triphenylphosphine was added to this complex, the signal due to the maleic anhydride protons collapsed to a sharp singlet (δ 3.95 ppm). This disappearance of P–H coupling would imply rapid exchange between the free and coordinated phosphines. When one mole of maleic anhydride was added, no exchange of olefin was observed.

The NMR spectral data of several palladium(0) maleic anhydride complexes prepared here are summarized in Table 1. In those complexes other than with L= triphenylphosphine, only two lines were observed which can be assigned to the most intense lines in the AA'XX' system. The effect of phosphorus ligands on the chemical shift of the maleic anhydride protons will be discussed later.

TABLE 1

NMR SPECTRA OF L_2Pd(MALEIC ANHYDRIDE)[a] (60 MHz)

L	*δ(maleic anhydride)*[b]	*δ(phenyl)*	*δ(methyl)*	$J(P-H)_{cis}+J(P-H)_{trans}$
(p-CH$_3$OC$_6$H$_4$)$_3$P	4.06	6.5–7.6	3.24 s	6
CH$_3$(C$_6$H$_5$)$_2$P	3.95	6.8–7.5	1.60 d (J 7 Hz)	6
(C$_6$H$_5$)$_3$P	3.93	6.8–7.5		4.4
(p-ClC$_6$H$_4$)$_3$P	3.79	6.7–7.2		4
(C$_6$H$_5$O)$_3$P	3.31	6.8–7.3		6
CH$_3$C(CH$_2$O)$_3$P	3.43		1.04 s	4

[a] In benzene-d_6 solution at 34°; δ in ppm relative to internal TMS, and J in Hz; s singlet, d doublet. [b] Free maleic anhydride shows a resonance at δ 5.34 ppm in benzene-d_6.

TABLE 2

ν(CO) OF MALEIC ANHYDRIDE IN L_2Pd(MALEIC ANHYDRIDE)[a] (cm^{-1})

L	ν*(CO)*		$\Delta\nu$*(CO)*			ν*(CO)* (A_1) *of* $Ni(CO)_3L^e$
	ν^1	$\nu_2{}^b$	$\nu_1 f^c - \nu_1$	$\nu_2 f^d - \nu_2$	$\nu_1 - \nu_2$	
$(p\text{-}CH_3OC_6H_4)_3P$	1802	1738	44	46	64	2066.1
$CH_3(C_6H_5)_2P$	1800	1736	46	48	64	2067.0
$(C_6H_5)_3P$	1806	1743	40	41	63	2068.9
$(p\text{-}ClC_6H_4)_3P$	1806	1744	40	40	62	2072.8
$(C_6H_5O)_3P$	1813	1751	33	33	62	2085.3
$CH_3C(CH_2O)_3P^f$	1814	1755	32	29	66	2087.3
Free maleic anhydride	1846	1784			62	

[a] Measured in THF solution using 0.1 mm liquid cell (NaCl). [b] This band contains a weak shoulder. [c] $\nu_1 f = 1846$ cm^{-1}. [d] $\nu_2 f = 1784$ cm^{-1}. [e] Quoted from ref. 12. [f] Due to the low solubility in THF, the sharp absorption bands were not obtained.

Infrared spectra

Infrared spectral data are given in Table 2. Free maleic anhydride shows carbonyl absorption bands at 1846 and 1784 cm^{-1} in THF solution; the latter band is more intense. With coordination of maleic anhydride to palladium, the splitting of the ν(CO) band showed no essential change, while the intensities of the two bands became approximately equal and the low frequency band is accompanied by a weak shoulder at a somewhat higher frequency. In the platinum(0) quinone complexes the splitting of the ν(CO) band is reported to increase with coordination[11].

As is usual with olefin complexes of zerovalent transition metals, the ν(C=C)

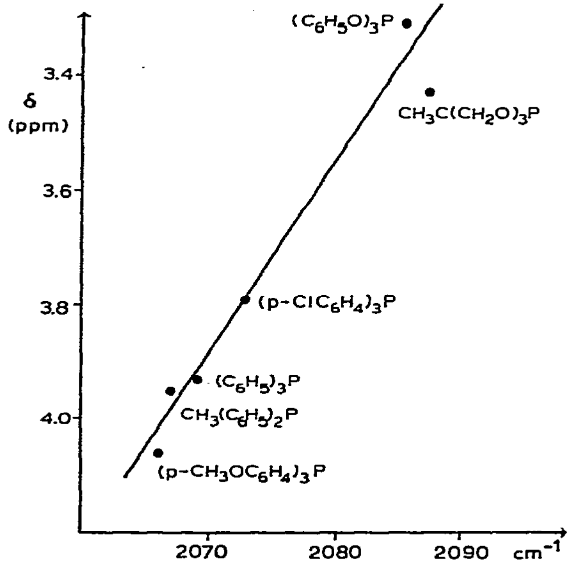

Fig. 4. Correlation between δ values of maleic anhydride protons in L_2Pd(maleic anhydride) and ν(CO) (A_1) of $Ni(CO)_3L$.

of maleic anhydride cannot be assigned owing to the large shift to lower wavenumbers. The most important feature of the spectra is that all complexes show shifts of ν(CO) to lower wavenumbers. As shown in Fig. 3, the degree of this shift can be correlated linearly with the A_1 carbonyl stretching frequency in the complex $Ni(CO)_3L$, which provides an estimate of the donor–acceptor ability of the phosphorus ligand, L[12].

Many instances are known[2,11,13–15] where the stretching frequencies of unsaturated groups, such as carbonyl and nitrile directly bound to the double bond, show shifts to the lower wavenumbers upon olefin coordination to transition metals. The relatively small shift (29–48 cm^{-1}) would imply that there is no direct bonding between the carbonyl groups and palladium in all the complexes studied here.

Recently, Ugo *et al.*[15] proposed that the shift to lower wavenumbers could be explained by a polarization of the unsaturated electronegative group due to population of the π^*-antibonding orbitals of the olefin. The results obtained here may also be interpreted in terms of this concept, since the phosphorus ligands, which are good σ-donors and poor π-acceptors, will lead to an increase in electron density on palladium and, in consequence, enhance π-back-donation to the olefin ligands.

Similar results have been reported by Maitlis *et al.*[16] who studied zerovalent acetylene complexes. The magnitude of the shift of the acetylenic band to lower wavenumbers [$\Delta\nu(C{\equiv}C)$] in the series $(R_3P)_2M(CF_3C{\equiv}CCF_3)$ increases in the order, $Ph_3P < Ph_2MeP < n\text{-}Bu_3P$, for both $M = Pd$ and Pt. It is obvious that this order can be attributed to the ease of back donation from the metal to the π^*-antibonding orbitals of the acetylene ligand.

Chemical shift of the maleic anhydride protons

The signals of the maleic anhydride protons are shifted to higher field in all complexes. These shifts (Fig. 4) are linearly related to the A_1 carbonyl stretching frequencies of the aforementioned complex, $Ni(CO)_3L$.

It is a well known phenomenon[17] that the signals of olefinic protons experience a high field shift upon complexation with transition metals*. The source of this high field shift is not fully understood at present. In general, however, olefins coordinated with transition metals of lower oxidation states always show larger high field shifts.

Recently, it has been proposed[15] that this shift can be directly related to the amount of π back-donation and consequent distortion from planarity of the olefin geometry. If so, the chemical shift could be used as a convenient criterion for estimating the strength of the olefin-to-metal bond.

Contrary to this concept, the present study shows that the signals of maleic anhydride protons move to higher field as the basicity of the phosphorus ligands decreases. Similar results have been obtained for L_2Pd(dimethyl fumarate) complexes. The δ values of olefinic protons decrease in the order (in benzene-d_6); $(C_6H_5)_3P$, δ 4.84 ppm > $(p\text{-}ClC_6H_4)_3P$, δ 4.63 ppm > $(C_6H_5O)_3P$, δ 4.16 ppm.

This trend is exactly the reverse of that observed in a series of *trans*-$PtCl_2$(*para*-substituted pyridine-*N*-oxide) (C_2H_4) complexes[1], in which more strongly electron-releasing substituents, such as $-OCH_3$ and $-OCH_2C_6H_5$, give rise to larger high field

---

* In silver(I)–olefin complexes, slight shifts to lower field have been observed exceptionally[18].

shifts in the olefinic protons; the greatest difference in chemical shift among these complexes being 0.36 ppm. In this system, π back-donation from divalent platinum to ethylene seems to be a main factor accounting for the high field shifts.

In the zerovalent system studied here, it is difficult to explain the high field shift only in terms of π back-donation. Additional factors may influence the chemical shift of the maleic anhydride protons. The direct influences (through space) of ring currents, induced by the phenyl groups of the phosphorus ligands, may be eliminated because the ligand $CH_3C(CH_2O)_3P$ which has no phenyl groups shows the same tendency as the other ligands. The diamagnetic anisotropy of the carbonyl groups in maleic anhydride itself must be taken into consideration. We can, however, safely exclude this effect, since a model of maleic anhydride shows that a decrease of carbon–oxygen bond order will give rise to the high field shift of olefinic protons[19], which is inconsistent with the fact that the more basic phosphorus ligand causes the smaller high field shift. These considerations lead us to postulate that in these zerovalent complexes, σ-donation from olefin to metal is a more important contributing factor to the high field shift than the π back-donation. The consumption of the π-electrons of olefin for the σ-bonding will decrease the deshielding of the olefinic protons[20].

At the present time, it seems rather unwise to assume that the high field shift of signals of olefinic protons are simply governed by π back-donation from metal to olefin irrespective of the oxidation state or the numbers of *d*-electrons of the central metal.

EXPERIMENTAL

Infrared spectra were recorded on a Jasco Model DS-402G spectrophotometer. NMR spectra were measured on a Hitachi–Perkin–Elmer R-20 (60 MHz) and a Jeol JNM 4H-100 (100 MHz) instruments in C_6D_6 under nitrogen. For the complex, $[CH_3C(CH_2O)_3P]_2Pd$(maleic anhydride), an accumulative technique was used because of its low solubility in C_6D_6.

TABLE 3

PROPERTIES AND ANALYTICAL DATA FOR L_2Pd(MALEIC ANHYDRIDE)

L	*Color*	*M.p.*[a] (°C)	*Analysis found (calcd.) (%)*			*Mol. wt. found*[b] *(calcd.)*
			C	*H*	*P*	
$(p\text{-}CH_3OC_6H_4)_3P$	Yellow	163–165	61.27 (60.77)	4.87 (4.88)	7.14 (6.81)	885[c] (909)
$CH_3(C_6H_5)_2P$	Yellow	154–157	59.86 (59.57)	4.95 (4.67)	10.34 (10.24)	606[d] (605)
$(p\text{-}ClC_6H_4)_3P$	Pale yellow	137–138	52.15 (51.34)	2.78 (2.80)	6.78 (6.62)	892[c] (936)
$(C_6H_5O)_3P$	Colorless	135–137	57.80 (58.23)	3.68 (3.91)	7.82 (7.51)	814[d] (825)
$CH_3C(CH_2O)_3P$[e]	Colorless	227–235	30.58 (30.77)	3.74 (3.79)	10.82 (10.58)	506[c] (500)[f]

[a] All complexes melt with decomposition. [b] Measured by vapor pressure osmometry. [c] Dichloromethane solution. [d] Benzene solution. [e] Calculated as $[CH_3C(CH_2O)_3P]_2Pd$(maleic anhydride)·CH_2Cl_2 Found: Cl, 11.82. Calcd.: Cl, 12.11%. [f] Value excluding methylene chloride.

Materials

Starting materials, PdL_4 [$L = (p\text{-}CH_3OC_6H_4)_3P$, $CH_3(C_6H_5)_2P$ and $CH_3C(CH_2O)_3P$], were prepared by methods described in the literature[21,22], whilst the complexes, $Pd[(p\text{-}ClC_6H_4)_3P]_3$[21] and $Pd[(C_6H_5O)_3P]_4$[21], were obtained by reduction[23] of $(\pi\text{-}C_3H_5PdCl)_2$ in the presence of the appropriate phosphines in benzene with trimethylsilane and lithium aluminum hydride, respectively.

Preparation of L_2Pd(maleic anhydride)

All maleic anhydride-coordinated palladium complexes were prepared by replacement reactions between maleic anhydride and the corresponding tris- or tetrakis (tertiaryphosphine)palladium complexes. The preparation of $[(C_6H_5)_3P]_2$-Pd(maleic anhydride) has been described in an earlier report[2]. Other complexes were also prepared by essentially same method. A typical procedure is as follows: to a solution of $Pd[(p\text{-}CH_3OC_6H_4)_3P]_4$ (690 mg, 0.455 mmol) in 20 ml of benzene, maleic anhydride (80 mg, 0.815 mmol) in 5 ml of tetrahydrofuran was added under pure nitrogen at ambient temperature. After stirring the mixture for 2.5 h, the solution was filtered, then methanol (10 ml) and n-hexane (85 ml) were added. On refrigeration, the solution yielded yellow crystals of $[(p\text{-}CH_3OC_6H_4)_3P]_2Pd$(maleic anhydride), which were washed with methanol and then with a mixture of benzene/hexane (1/1), and dried *in vacuo* (368 mg, 89% yield).

In the solid state, all complexes are stable in air for many hours. Physical properties and analytical data of new complexes obtained here are shown in Table 3.

REFERENCES

1 P. D. Kaplan and M. Orchin, *Inorg. Chem.*, 4 (1965) 1319.
2 S. Takahashi and N. Hagihara, *J. Chem. Soc. Jap.* (*Pure Chem. Sect.*), 88 (1967) 1306.
3 S. Takahashi, T. Shibano and N. Hagihara, *Bull. Chem. Soc. Jap.*, 41 (1968) 454.
4 J. W. Emsly, J. Feeney and L. H. Sutcliffe, *High Resolution Nuclear Magnetic Resonance Spectroscopy*, Pergamon, New York, N. Y., 1966, p. 396.
5 J. N. Francis, A. McAdam and J. A. Ibers, *J. Organometal. Chem.*, 29 (1971) 131.
6 A. McAdam, J. N. Francis and J. A. Ibers, *J. Organometal. Chem.*, 29 (1971) 149.
7 C. Panattoni, G. Bombieri, U. Bellco and W. H. Baddley, *J. Amer. Chem. Soc.*, 90 (1968) 798.
8 C. D. Cook, C. H. Koo, S. C. Nyburg and M. T. Shiomi, *Chem. Commun.*, (1967) 426.
9 P. T. Cheng, C. D. Cook, S. C. Nyburg and K. Y. Wan, *Inorg. Chem.*, 10 (1971) 2210.
10 K. S. Wheelock, J. H. Nelson, L. C. Cusachs and H. B. Jonassen, *J. Amer. Chem. Soc.*, 92 (1970) 5110.
11 S. Cenini, R. Ugo and G. La Monica, *J. Chem. Soc. A*, (1971) 416.
12 C. A. Tolman, *J. Amer. Chem. Soc.*, 92 (1970) 2953.
13 G. N. Schrauzer, *J. Amer. Chem. Soc.*, 82 (1960) 1009.
14 E. Weiss, K. Stark, J. E. Lancaster and H. D. Murdoch, *Helv. Chim. Acta.*, 46 (1963) 288.
15 S. Cenini, R. Ugo and G. La Monica, *J. Chem. Soc. A*, (1971) 409.
16 E. O. Greaves, C. J. L. Look and P. M. Maitlis, *Can. J. Chem.*, 46 (1968) 3879.
17 M. L. Madox, S. L. Stafford and H. D. Kaesz, *Advan. Organometal. Chem.*, 3 (1965) 1.
18 H. W. Quinn, J. S. McIntyre and D. J. Peterson, *Can. J. Chem.*, 43 (1965) 2896.
19 L. M. Jackman and S. Sternhell, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, Pergamon, New York, 2nd ed., 1969, p. 88.
20 M. A. Bennett, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, (1961) 2037.
21 L. Malatesta and M. Angoletta, *J. Chem. Soc.*, (1957) 1186.
22 R. L. Keiter and J. G. Verkade, *Inorg. Chem.*, 9 (1970) 404.
23 S. Takahashi, T. Shibano, H. Kojima and N. Hagihara, *Organometal. Chem. Syn.*, 1 (1970/1971) 193.