Table I. Reaction Pathways with Methyl Formate[a]

| | proton abstraction, % | carbonyl addition, % | $S_N2$ displacement, % |
|---|---|---|---|
| $H^{18}O^-$ | 61 | 34 | 5 |
| $HOO^-$ | 64 | 28 | 8 |

[a] Both nucleophiles react at the collision rate $k = 2.0 \times 10^{-9}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for $HO^-$ and $1.9 \times 10^{-9}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for $HOO^-$. The initial product distributions were obtained by extrapolating product percentages to zero neutral flow.

measured the rate of its reaction with methyl fluoride and found it to be somewhat less reactive than either $HO^-$ or $CH_3O^-$, as would be predicted from its lesser basicity; it therefore displays no detectable $\alpha$-effect in this $S_N2$ reaction. However the rate differences are small, and the results could hardly be considered as conclusive, particularly since the energy available for reaction in each case (the ion–dipole binding energy in the reaction complex between the anion and methyl fluoride) will not necessarily be the same for each nucleophile.

A more stringent test would involve a comparison of relative rates among competing reaction channels within a single reaction complex. For this purpose methyl formate is the ideal neutral substrate, for it reacts with bases in three competitive ways, by proton abstraction (eq 1), by $B_{AC}2$ addition to the carbonyl (eq 2), and by $S_N2$ displacement on methyl (eq 3).[11] The first of these reactions should not be influenced by the $\alpha$-effect, while the latter two reactions should be. We have therefore compared the branching ratios for the reactions[12] of $H^{18}O^-$ and $HOO^-$ with methyl formate in the gas phase by using both a flowing afterglow apparatus and a recently constructed selected ion flow tube (SIFT).[13] The results are collected in Table I.[14]

$$HX^- + HC(O)OCH_3 \rightarrow [HXH\ \bar{C}(O)OCH_3] \rightarrow HXH{\cdot}OCH_3^- + CO \quad (1)$$

$$\rightarrow HC(O)X^- + CH_3OH \quad (2)$$

$$\rightarrow HC(O)O^- + CH_3XH \quad (3)$$

The rate-determining step in both of these processes is the collision between the ion and the neutral; once the reaction complex is formed, both reactions proceed to completion. However, the relative rates of proton abstraction, nucleophilic addition to the carbonyl group and $S_N2$ displacement on the methyl group, are the same for the two anions. Thus $HOO^-$ shows no enhanced nucleophilic reactivity compared to $HO^-$ in the gas phase, and we conclude that the $\alpha$-effect is most likely a manifestation of solvent effects.

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**Registry No.** $HOO^-$, 14691-59-9; $H^{18}O$, 65553-37-9; methyl formate, 107-31-3.

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[11] Takashima, K.; Riveros, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 6128–6132.

[12] The isotope tracer was necessary to distinguish the products in eq 2 and 3.

[13] Grabowski, J. J.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.*, in press.

[14] The experiments were carried out at room temperature and at 0.3 torr of He. For reactions of $HOO^-$ three ions corresponding to the products of eq 1–3 were the only products. Reactions with $HO^-$ are more exothermic, and two additional ions, $CH_3O^-$ (22%) and M-1 (17%) also appear. $CH_3O^-$ could arise either from reaction 1 or 2; following Riveros we assign it to (1). If it arises from (2), our conclusions are strengthened. $HO^-$ but not $HOO^-$ is strong enough a base to abstract a proton from the ester to form the M-1 ion. Our conclusions are not affected if some or all of the M-1 ion results from proton abstraction from the methyl group (see: Bartmess, J. E.; Caldwell, G.; Rozeboom, M. D. Presented at the 30th Annual Conference on Mass Spectrometry and Allied Topics; Honolulu, HI, June 6–11, 1982.

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# First In-Plane Coordination of a Simple Monoolefin in a Square-Planar Complex. Molecular Structure of $\eta^3$-Methallyl(triphenylphosphine)(styrene)platinum(II) Cation

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The C=C bond of an olefinic ligand in square-planar, d$^8$ metal-olefin complexes has generally been accepted,[1,2] except for (5-methylenecycloheptene)platinum dichloride,[3] to lie perpendicular to the coordination plane. The reason for the perpendicular or "upright" coordination was ascribed[2] primarily to unfavorable steric interactions with the cis ligands in the parallel or "in-plane" one. Such steric interactions also constitute a major portion of the olefin rotation barrier.[2] We have recently found that such barriers in $[Pt(\eta^3\text{-}CH_2CMeCH_2)(PPh_3)(olefin)]PF_6$ (**1**[4a] olefin = $CH_2{=}CH_2$, **1a**; (*E*)-MeCH=CHMe, **1b**) are remarkably low for a Pt(II)–olefin complex,[4b] suggesting very small steric requirements around the olefin. In addition to this, $^1$H NMR aspects of **1c** (olefin = $CH_2{=}CHPh$; see later) greatly different from those of $[Pd(\eta^5\text{-}C_5H_5)(PPh_3)(CH_2{=}CHPh)]PF_6$ (**2**),[5] of which the crystallographic study had revealed[6] the upright coordination of styrene, prompted us to undertake X-ray structural studies of the complexes of type **1**. We describe here the molecular structure of **1c**, which shows the first in-plane coordination of simple monoolefins in square-planar complexes.

The crystals of **1c** belong to the monoclinic system, space group *P*2$_1$/*n* with unit cell dimensions $a$ = 15.560 (3) Å, $b$ = 11.342 (3) Å, $c$ = 17.594 (3) Å, and $\beta$ = 110.91 (2)°; $d_c$ = 1.744 g cm$^{-3}$ for $Z$ = 4.[7] This crystal is isomorphous with that of **2**[6] although the metal and the ancillary ligand are different in these two. The structure was solved[8] by the use of that of **2** and refined aniso-

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[†] Department of Applied Chemistry.

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[1] Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33.

[2] Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801.

[3] Wright, L. L.; Wing, R. M.; Rettig, M. F.; Wiger, G. R. *J. Am. Chem. Soc.* **1980**, *102*, 5950. In this case chelate coordination of two C=C bonds in the ligand molecule compelled the exocyclic one to lie parallel to the coordination plane.

[4] (a) Kurosawa, H.; Asada, N. *J. Organomet. Chem.* **1981**, *217*, 259, and unpublished results. (b) $\Delta G^\ddagger_{rot}$ for **1b** at −55 °C (11.0 kcal/mol) may be compared to those[4c] of $PtCl(C_4H_8)(acac)$ (15.8 kcal/mol) and $PtCl_2(C_4H_8)(AsEt_3)$ (≥16 kcal/mol). No frozen 100-MHz $^1$H NMR spectra were obtained for **1a** down to −90 °C. However, assuming a chemical shift difference of two protons undergoing site-exchange as 0.5 ppm leads us to calculate $\Delta G^\ddagger_{rot}$ for **1a** at −90 °C as 8.8 kcal/mol. Such chemical shift difference of 0.5 ppm may be a minimum estimate for a complex bearing $PPh_3$, which exerts a large magnetic anisotropy effect to nearby protons.[4d,5] (c) Ashley-Smith, J.; Douek, Z.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1974**, *128*; (d) **1972**, 1776.

[5] Kurosawa, H.; Majima, T.; Asada, N. *J. Am. Chem. Soc.* **1980**, *102*, 6996.

[6] Miki, K.; Shiotani, O.; Kai, Y.; Kasai, N.; Kanatani, H.; Kurosawa, H. *Organometallics*, in press. Unit cell dimensions of **2** are $a$ = 15.571 (4) Å, $b$ = 11.187 (2) Å, $c$ = 17.596 (3) Å, and $\beta$ = 107.71 (2)°.

[7] A well-shaped crystal with approximate dimensions 0.25 × 0.30 × 0.40 mm was selected for X-ray analysis. Intensity measurements were carried out on a Rigaku automated four-circle diffractometer using graphite monochromatized Mo K$\alpha$ radiation. Reflections with $2\theta$ up to 54.0° were collected by the $\theta$–$2\theta$ scan technique. The $2\theta$ scan rate was 4° min$^{-1}$ and the san width $\Delta 2\theta = (2.5 + 0.70 \tan \theta)°$. The background intensities were measured for 7.5 s at each end of a scan.•

[8] Because of isomorphism of crystals of **1c** with **2**, the structure of **1c** including the $PF_6$ anion was at first assumed essentially similar to that of **2** except for the methallyl moiety. The atomic coordinates of **2** except for the Cp group were employed for the initial atomic positional parameters of **1c**. By the isotropic refinement, parameters of these atoms were reasonably converged except for the C(1), C(2), and C(3) atoms of styrene ligand. This behavior of three carbon atoms was later confirmed due to the in-plane coordination of the styrene (see text). The locations of these divergent atoms as well as those of the remaining methallyl group were easily found in the subsequent difference Fourier maps.

0002-7863/83/1505-2482$01.50/0

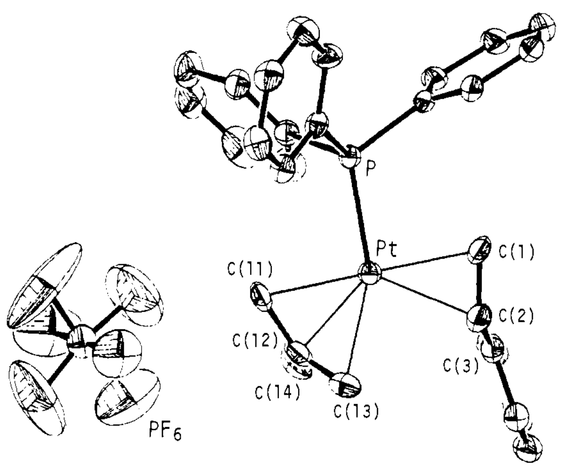

**Figure 1.** Molecular structure of $[\mathrm{Pt}(\eta^3\text{-}\mathrm{CH_2CMeCH_2})(\mathrm{PPh_3})(\mathrm{CH_2{=}CHPh})]\mathrm{PF_6}$ (**1c**).[10] Atoms are represented by thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and bond angles (deg) not cited in the text are Pt–P = 2.309 (3), C(1)–C(2) = 1.341 (17), C(2)–C(3) = 1.512 (17), C(12)–C(14) = 1.535 (21); P–Pt–C(1) = 88.2 (3), C(1)–Pt–C(2) = 34.6 (4), C(2)–Pt–C(13) = 79.8 (5).

tropically by the block-diagonal least-squares procedure to $R$ = 0.053 for 4919 reflections ($|F_o| > 3\sigma(|F_o|)$).[9]

The molecular structure of **1c** is shown in Figure 1. The internal geometry of the $\eta^3$-allyl ligand and its mode of coordination to Pt[11] seem to be normal when compared to those[12] in other $\eta^3$-allyl(phosphine) complexes of Pt(II) and Pd(II). Very remarkable is nearly in-plane coordination of the C=C bond with the phenyl substituent on the same side as that of the allyl methyl with respect to the coordination plane. The angle between the C=C axis and the approximate coordination plane, defined by the Pt, P, and the center of gravity of the allyl triangle, is only 10.0° (the corresponding angle in **2** is ca. 90°) with C(2) being displaced farther from the plane (0.32 Å) than C(1) (0.08 Å). The intrinsically small bite angle of the bidentate ligand ($\eta^3$-allyl) and the smaller angle of C(11)–Pt–P [92.1 (4)°] than usual C(allyl)–metal–cis-ligand angles appear to help make enough room for the in-plane coordination of the styrene in **1c**, even though both Pt–C(olefin) lengths [Pt–C(1) = 2.203 (12) Å, Pt–C(2) = 2.301 (12) Å] are somewhat longer than those in other sytrene complexes of Pt(II) [2.16–2.19 and 2.20–2.24 Å, respectively].[13]

$^1$H NMR data[4a,14] of **1c**, when compared with those[5,14] of **2**, seem to be consistent with preservation of the in-plane configuration or one close to it even in solutions.[15] Thus, in **2** the resonances due to $H^{gem}$ and $H^{tr}$, located close to $PPh_3$, receive considerable upfield shifts due to the magnetic anisotropy of the P-phenyl rings and exhibit $^{31}$P couplings, while in **1c** it is the $H^{tr}$ and $H^{cis}$ resonances that receive such anisotropy and exhibit $^{31}$P couplings. It should be pointed out that placing the styrene ligand in **1c** perpendicular to the coordination plane with the phenyl substituent on the allyl side, just as in **2**, requires no severe steric constraint.[16]

We presume that behind this contrast between the structures of **1c** and **2** are electronic demands of the ancillary hydrocarbon ligands. The nature of the metal atom seems less important in this argument, for $^1$H NMR evidence unambiguously indicated[5] the upright coordination of ethylene in $[\mathrm{Pt}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{PPh_3})(\mathrm{CH_2{=}CH_2})]\mathrm{ClO_4}$ (**3**). The role of the Cp ligand, a six-electron donor, in stabilizing the upright coordination of the olefin in **2** and **3** has already been pointed out.[5,6] The structure of **1c** determined might be a manifestation of the notion,[2,4c] in those complexes that lack severe steric constraints around the olefin, that the d$\pi$ orbital used for $\pi$ back-bonding in the in-plane coordination in square-planar complexes is slightly higher than that in the upright one. Or it is also possible that the lowest filled MO ($\pi$ type) of the allyl ligand extending to the central carbon raised the in-plane d$\pi$ orbital effectively, which is pointing near to this carbon.

The square-planar metal complexes simultaneously containing the $\eta^3$-allyl and olefin ligands have often been regarded as key intermediates in various metal-catalyzed synthetic reactions.[17] The results described above may thus be useful in planning and explaining the steric outcome of such synthetic reactions.

**Registry No. 1c**, 79730-88-4.

**Supplementary Material Available:** Table of fractional atomic coordinates and anisotropic thermal parameters for **1c** (1 page). Ordering information is given on any current masthead page.

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(9) The HBLS-V program was used for the refinement: Ashida, T. "The Universal Crystallographic Computing System-Osaka", 2nd ed.; Computation Center, Osaka University, 1979; p 53. The atomic scattering factors used were taken from "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol IV, p 72.

(10) Johnson, C. K. ORTEP-II, Oak Ridge National Laboratory: Oak Ridge, TN, Report ORNL-5138, 1976.

(11) Bond lengths (Å): C(11)–C(12) = 1.449 (19); C(12)–C(13) = 1.380 (19); Pt–C(11) = 2.175 (13); Pt–C(12) = 2.196 (14); Pt–C (13) = 2.226 (14). Bond angles (deg): C(11)–C(12)–C(13) = 116.4 (12); C(11)–Pt–C(13) = 66.3 (5). The dihedral angle between the approximate coordination plane (see below) and the $\eta^3$-allyl plane is 115.5°, and C(14) is displaced from the latter plane toward Pt by 0.34 Å.

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(14) The coordination shifts ($\delta_{free} - \delta_{complex}$) for $H^{gem}$, $H^{tr}$, and $H^{cis}$ (with respect to Ph) of styrene are as follows: **1c**, 0.17, 1.41, 1.49 ppm; **2**, 1.46, 1.97, 0.15 ppm. $J_P$ values (Hz) are as follows: **1c**, 3.0 ($H^{tr}$), 7.2 ($H^{cis}$); **2**, 3.0 ($H^{gem}$), 2.6 ($H^{tr}$).

(15) The following discussion is valid for the NMR data due to the major diastereoisomer[4a] in solutions. The olefinic proton resonances due to the minor isomer could not be resolved well.

(16) Although rotational isomerism is possible for **1c**, variable-temperature (−90 to 50 °C) $^1$H NMR spectra suggested[4a] that one rotamer predominates or almost excludes the other.

(17) (a) Maitlis, P. M. "The Organic Chemistry of Palladium"; Academic Press: New York, 1971; Vol. 1 and 2. (b) Jolly, P. W.; Wilke, G. "The Organic Chemistry of Nickel"; Academic Press: New York, 1975; Vol. 1 and 2. (c) Hosokawa, T.; Uno, T.; Inui, S.; Murahashi, S. *J. Am. Chem. Soc.* **1981**, *103*, 2318.

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# Observation of High-Resolution Oxygen-17 NMR Spectra of Inorganic Solids

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Oxygen is the most abundant element on earth, comprising over 60% of the atoms in the earth's crust, and is thus of considerable geological interest. We report in this communication the first observation of high-resolution oxygen-17 nuclear magnetic resonance spectra of several oxides and oxyanions, obtained at 11.7 T by using the techniques of magic-angle sample spinning (MASS[1,2]) and variable-angle sample spinning (VASS[3,4]) NMR

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(1) E. R. Andrew, *Int. Rev. Phys. Chem.*, **1**, 195 (1981); J. Schaefer and E. O. Stejskal, *J. Am. Chem. Soc.*, **98**, 1031 (1976).

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(3) S. Ganapathy, S. Schramm, and E. Oldfield, *J. Chem. Phys.*, **77**, 4360 (1982).

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