thoxyl (**6**). The yield was 0.8 g (40%): bp 115-117 °C (1.2 mm); NMR ($CDCl_3$) δ 1.0-2.05 (m, 4, CH_2), 3.25 (br s, 1, CH); IR (film) 2970 (CH), 2200, 2060 (CD), 1650 (C=C) cm^{-1}; mass spectrum (70 eV), *m/e* 290 (M^+), 288 ($M^+ - 2$), 292 ($M^+ - 2$). Anal. (undeuterated) Calcd for $C_8H_{12}OBr_2$: C, 33.83; H, 4.25. Found: C, 34.26; H, 4.18.

3-Methoxy-*d*$_3$-1-(dichloromethylene)cyclohexane-*2,2,4,4-d*$_4$ (3). To 0.4 g (10.4 mmol) of LiCl in 40 mL of dry THF at −78 °C was added 2.5 mL (5.2 mmol) of butyllithium under N_2. After 8 min of stirring, diethyl chloromethanephosphate (0.97 g, 5.2 mmol) was added, followed by 0.8 g (5.2 mmol) of CCl_4 and 0.7 g of 3-methoxy-*d*$_3$-cyclohexan-1-one-*2,2,4,4-d*$_4$ (5.2 mmol). The product was isolated as described for the compound lacking methoxyl (**7**). The crude yield was 2.6 g (50%). The pure compound was isolated by vapor-phase chromatography on a 5 ft × $^1/_4$ in. column, 20% Carbowax 20-M Chromosorb P 60/80: NMR (CCl_4) δ 0.7-2.8 (m, 4, CH_2), 3.2 (br s, 1, CH); IR (film) 2940 (CH), 2200, 2060 (CD), 1630 (C=C) cm^{-1}; mass spectrum (70 eV), *m/e* 201 (M^+), 167 ($M^+ - 34$). Anal. (undeuterated) Calcd for $C_8H_{12}OCl_2$: C, 49.25; H, 6.20. Found: C, 49.55; H, 6.26.

3-Methoxy-*d*$_3$-1-(isopropylidene)cyclohexane-*2,2,4,4-d*$_4$ (1). An ethereal solution of dimethylcopperlithium was prepared from 8.55 g (45 mmol) of cuprous iodide, 49 mL (83.25 mmol, 1.7 M solution in ethyl ether) of methyllithium, and 1.3 g (4.72 mmol) of 3-methoxy-*d*$_3$-1-(dibromomethylene)cyclohexane-*2,2,4,4-d*$_4$ as described for the compound lacking methoxyl (**5**).[5] The crude yield was 0.7 g (93%). The compound was purified by vapor-phase chromatography (see compound **3**): NMR (CCl_4) δ 1.1-2.3 (m, 4, CH_2), 1.67 (s, 6, CH_3), 3.1 (br s, 1, CH). Anal. (undeuterated) Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 76.63; H, 11.64.

3-Methoxy-*d*$_3$-1-(dicyanomethylene)cyclohexane-*2,2,4,4-d*$_4$ (4) was prepared from 0.35 g (2.55 mmol) of 3-methoxy-*d*$_3$-cyclohexan-1-one-*2,2,4,4-d*$_4$ and malononitrile (0.17 g, 2.55 mmol):[5] 0.3 g (64%); bp 139-140 °C (0.7 mm); NMR (CCl_4) δ 1.6-2.0 (m, 2, CH_2), 3.4 (br s, 1, CH); IR (film) 2940, 2890 (CH), 2240 (C≡N), 2200, 2060 (CD), 1670 (C=C) cm^{-1}; mass spectrum (10 eV), *m/e* 183 (M^+).

Acknowledgment. We wish to thank Dr. Michael N. Paddon Row for helpful suggestions.

Supplementary Material Available: The archival version of this paper includes Scheme I, discussions of the relative contributions of induction and resonance to the $C{=}CX_2$ dipole and dipole-quadrupole interactions, Table III, and further experimental details (13 pages). Ordering information is given on any current masthead page.

Stereochemistry and Mechanisms of Reactions of Dioxygen Complexes with Organic Electrophiles as Studied by Use of Chiral Reagents and Isotopic Labeling

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Abstract: From reactions of PtO_2L_2 (L = PPh_3, $P(c\text{-}C_6H_{11})_3$) with 1 mol of triphenylmethyl bromide or benzoyl bromide the corresponding (alkylperoxo)platinum(II) complexes $L_2PtBr(OOR)$ (**1a**, L = PPh_3, R = CPh_3; **1b**, L = $P(c\text{-}C_6H_{11})_3$, R = CPh_3; **2**, L = PPh_3, R = COPh) were isolated, which were well characterized by elemental analysis and IR spectroscopy. The complex **1a,b** or **2** was treated with another mole of organic halides to give the corresponding dialkyl peroxides ($Ph_3COOCPh_3$, PhC(O)OOC(O)Ph) in good yields. Thus, the stepwise mechanism proposed previously for "metal-assisted peroxidations" was verified. A similar reaction of $PtO_2(PPh_3)_2$ with an optically active (*S*)-(−)-α-phenethyl bromide produced a peroxoplatinum(II) complex, $PtBr(OOCH(CH_3)Ph)(PPh_3)_2$ (**3**), which gave upon acidolysis (*R*)-(+)-α-phenethyl hydroperoxide. Reductive cleavage of **3** with $NaBH_4$ gave (*R*)-(+)-α-phenethyl alcohol. Hence, it can be concluded that the reaction of PtO_2L_2 with organic halides proceeds via the S_N2-type transition state. From the IR ^{18}O isotopic shifts the O-O stretching band was assigned for the products from the reactions of PtO_2L_2 with acetone (**4**), benzophenone (**5**), 1,1-dicyano-2-methylpropene (**8**), and tetracyanoethylene (**9**). The ^{18}O IR study also shows that the peroxy bond involved in these products is derived from PtO_2L_2. The reaction product $\overline{PtO(CH_3OOC)C{=}CO}(COOCH_3)L_2$ (**10a**, L = PPh_3; **10b**, L = $P(c\text{-}C_6H_{11})_3$) obtained from PtO_2L_2 and $CH_3OOCC{\equiv}CCOOCH_3$ was also studied by ^{18}O isotopic IR and ^{13}C NMR spectra. Acidolysis of **10b** gave dimethyl dihydroxymaleate in a good yield. Thus it was established that the reaction of an electrophilic acetylene with PtO_2L_2 results in the O-O bond cleavage.

Reactivities of the η^2-dioxygen ligand of low-valent later transition-metal complexes have received considerable investigations.[1] The nature of the $M(\eta^2\text{-}O_2)$ bonding was a subject of several theoretical studies.[2] These studies on $M(\eta^2\text{-}O_2)L_2$ (M = Ni, Pd, Pt) indicate that a considerable charge is transferred to the O_2 ligand. This is reflected in the facile reactions of $M(\eta^2\text{-}O_2)L_2$ (M = Ni, Pd; L = *t*-BuNC) with various electrophiles as we reported previously.[3] One of the nucleophilic reactions of $M(\eta^2\text{-}O_2)L_2$ is the "metal-assisted peroxidation" reaction[3] (eq 1).

$$2RX + Ni(O_2)(t\text{-}BuNC)_2 \rightarrow NiX_2(t\text{-}BuNC)_2 + ROOR \qquad (1)$$

A closely related reaction is the formation of hydrogen peroxide from acidolysis of $M(\eta^2\text{-}O_2)L_2$ (e.g., M = Ni, Pt; L = PPh_3).[4-6] The mechanisms of these peroxidation reactions still remain to be elucidated.

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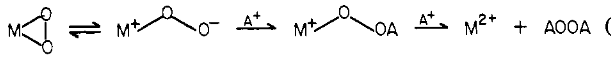
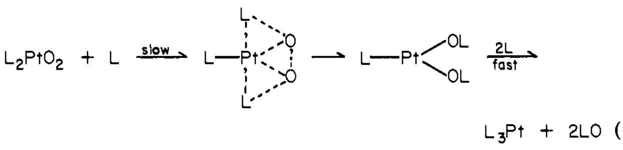
We postulated a consecutive reaction pathway (eq 2) on the


(2)

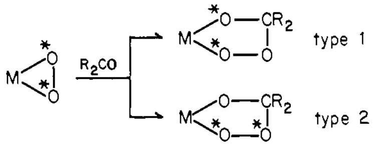
basis of symmetry consideration.[3] It was not possible then, however, to exclude the alternative mechanism, a concerted insertion of electrophiles into $M(\eta^2\text{-}O_2)$ bonds. For oxygenation of tertiary phosphines with $PtO_2(PR_3)_2$, a concerted mechanism was postulated some years ago by Halpern et al.[7] (eq 3). The

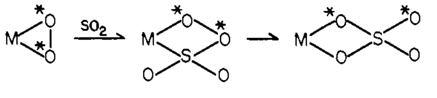

(3)

mechanism was revised in their more recent paper[8] which proposed a multistep process involving incipient formation of a free peroxide (a chain carrier) derived from a trace of protic impurities (eq 4).

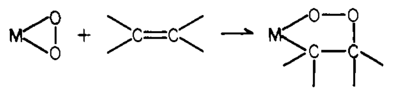
$$(PR_3)_2PtO_2 \xrightarrow[R'OH]{PR_3} Pt(PR_3)_4^{2+} + HO_2^- + R'O^- \qquad (4)$$

Two reaction schemes are conceivable for attack of an electrophile: direct attack on the O_2 ligand resulting in the O–O cleavage (type 1, eq 5) and insertion into the M–O bond retaining the O–O bond (type 2, eq 5). The reaction of SO_2 with $IrO_2Cl(PPh_3)_2$ leading to the corresponding sulfato complex was studied by Collman et al.[9] who concluded the insertion into a $M\text{–}O_2$ bond on basis of isotopic IR study (eq 6). Pathways for the reactions with various carbonyl compounds[6b,10,11] were a subject of debate. Ugo et al.[10a] once favored reaction type 1 in view of a possible description of the dioxygen ligand in terms of a polarized excited $O_2(^3\Sigma_u^-)$. Later, they favored[6b,10b,c] type 2 on the basis of the kinetic data, which cannot be regarded as unequivocal evidence. Although reactions of $PtO_2(PPh_3)_2$ with various carbonyl compounds have been studied rather extensively, definite assignments for the O–O stretching band of the perketyl species $\overline{MOOC(R_2)O}$ have not been achieved. Recently Roundhill et al.[12] suggested the pathway of type 2 for the reaction of iridium–dioxygen complex with hexafluoroacetone on the basis of the kinetics and IR spectra of the products containing isotopically labeled oxygen. The O–O stretching band, however, remained to be identified.

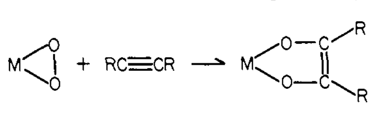

(5)


(6)

The reactions of the metal–dioxygen complex with olefins was also a subject of extensive studies.[13-21] Most of the attempted catalytic reactions appear to proceed through radical chain reactions.[13-18] Recent reports on the catalytic oxidation of terminal olefins with rhodium complexes such as $[RhO_2(AsPh_3)_4]^+$ or $RhCl(PPh_3)_3$[19-21] postulated a five-membered peroxo metallocyclic intermediate (eq 7). A similar cyclic peroxo complex was isolated from the reaction of tetracyanoethylene with $MO_2(PPh_3)_2$ (M = Pd, Pt).[22] Although the ^1H and ^{13}C NMR spectra are consistent with those of the metallocycle, direct evidence for the presence of an O–O bond had not been obtained. These previous works prompted us to reinvestigate the pathways of these nucleophilic metal–dioxgen reactions through isotopic IR studies.


(7)

The reaction of PtO_2L_2 ($L = P(c\text{-}C_6H_{11})_3$) with electrophilic acetylene like MeOOCC≡CCOOMe reported by Clark et al.[23]


(8)

(eq 8) is rather unique. If their structural assignment of the product is correct, the reaction represents a rare example for the reaction of type 1. We felt that the procuct has not been fully characterized. In this paper, therefore, we also add results of our studies on the reaction of acetylenes.

Results and Discussion

Reactions with Organic Halides. No intermediate complex could be detected in the reactions of organic halides with $Ni(O_2)(t\text{-}BuNC)_2$ due to its rapid reaction even at −78 °C,[3] whereas the reactions with PtO_2L_2 ($L = PPh_3$ or $P(c\text{-}C_6H_{11})_3$) were more controllable. Thus we could isolate alkylperoxo compounds (**1a**,**b**, **2**) in good yield from the reaction carried out at −20 °C employing 1 mol of organic halides (eq 9).

$$PtO_2L_2 + RBr \rightarrow L_2PtBr(OOR) \qquad (9)$$

1a, $R = CPh_3$, $L = PPh_3$
1b, $R = CPh_3$, $L = P(c\text{-}C_6H_{11})_3$
2, $R = COPh$, $L = PPh_3$

These complexes were characterized by elemental analysis, molecular weight measurements, and IR spectroscopy of the isotopic derivatives. The characteristic intense IR band due to O–O stretching in the parent PtO_2L_2 complexes appears in the region 815–825 cm^{-1} and shifts to higher frequency (Δ = 6–42 cm^{-1}) with a concomitant decrease in intensity upon formation of the alkylperoxy species. Although the difference in spectral features is marked, we felt that an unambiguous assignment of the weak IR band to an O–O stretch in the C–OO–M fragment

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Table I. ^{18}O Isotope IR Bands (cm^{-1}) of Oxygenated Platinum Complexes[a]

complex	$^{16}O-^{16}O$	$^{16}O-^{18}O$	$^{18}O-^{18}$	$M-^{16}O$	$M-^{18}O$	others
$PtBr(OOCPh_3)(PPh_3)_2 \cdot CH_2Cl_2$ (1a)	831		791	364 321	355 313	
$PtBr(OOCPh_3)[P(c\text{-}C_6H_{11})_3]_2$ (1b)	821		788			
$PtBrOOC(O)Ph(PPh_3)_2$ (2)	867		846			1734 (ν(C=O))
$PtOOC(O)(CH_3)_2(PPh_3)_2$ (4a)	811	793	786	379	371	
$PtOOC(O)(CH_3)_2[P(c\text{-}C_6H_{11})_3]_2$ (4b)	795		762	383	376	
$PtOOC(O)O[P(c\text{-}C_6H_{11})_3]_2$ (6)	822		803	378	371	1680 (ν(C=O))
$PtOOC(CH_3)_2C(CN)_2(PPh_3)_2$ (8a)	813	798	775	371	366	2216 2205 (ν(C≡N))
$PtOOC(CH_3)_2C(CN)_2[P(c\text{-}C_6H_{11})_3]_2$ (8b)	820		789	369	363	2214 2203 (ν(C≡N))
$PtOOC(CN)_2C(CN)_2(PPh_3)_2$ (9a)	811		767	390	383	2225 2211 (ν(C≡N))
$PtOOC(CN)_2C(CN)_2[P(c\text{-}C_6H_{11})_3]_2$ (9b)	821		783	392	386	2220 2210 (ν(C≡N))
$PtO(H_3COOC)C{=}CO(COOCH_3)(PPh_3)_2 \cdot CH_2Cl_2$ (10a)						1735 1697 (ν(C=O)) 1583 (ν(C=C))
$PtO(H_3COOC)C{=}CO(COOCH_3)[P(c\text{-}C_6H_{11})_3]_2$ (10b)						1734 1713 (ν(C=O)) 1584 (ν(C=C))
$PtO(H_3C)C{=}CO(CN)[P(c\text{-}C_6H_{11})_3]_2$ (11)						2173 (ν(C≡N)) 1610 1605 (ν(C=C))

[a] Measured in Nujol mull.

required isotopic studies. Accordingly, the IR spectrum of **1a**, prepared from PtO_2L_2 containing $^{18}O_2$ (99%), was examined in two regions corresponding to the O–O (700–900 cm^{-1}) and Pt–O stretching (300–400 cm^{-1}). A weak band near 831 cm^{-1} and two bands at 364 and 321 cm^{-1} shifted to new peaks at 791, 355, and 313 cm^{-1}, respectively. Hence, the origin of the 831-cm^{-1} band may be ascribed to a vibrational mode whose potential function distribution heavily lies on the O–O stretching. Similarly the two low-frequency bands at 364 and 321 cm^{-1} are considered to be associated with the Pt–O stretching. The 821-cm^{-1} band of **1b** shifts to 788 cm^{-1} upon ^{18}O labeling (Table I).

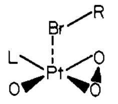
Two isotopic shifts from 867 to 846 cm^{-1} and from 840 to 827 cm^{-1} were observed in complex **2** (Table I). Since the 840-cm^{-1} band can be seen for $PtBrOC(O)Ph(PPh_3)_2$ containing ^{18}O (vide infra), the band at 867 cm^{-1} may be assigned to a vibration essentially associated with the O–O stretching. In the low-frequency region of **1b** and **2**, clear isotopic bands could not be detected. However, the presence of a peroxo linkage (Pt–O–O–R) in these complexes is doubtless as the reaction with another mole of organic halides produces the corresponding dialkyl peroxide in over 60% yield (eq 10). The yield of isolated dibenzoyl peroxide

$$PtBr(OOR)L_2 + RBr \rightarrow cis\text{-}PtBr_2L_2 + ROOR \qquad (10)$$

$$\begin{array}{l} \mathbf{1a},\ R = CPh_3,\ L = PPh_3 \\ \mathbf{1b},\ R = CPh_3,\ L = P(c\text{-}C_6H_{11})_3 \\ \mathbf{2},\ R = COPh,\ L = PPh_3 \end{array}$$

was low (22%) apparently due to its instability in a solution containing metal salts. These reactions produce *cis*-dibromoplatinum complex (ν(Pt–Br) 219 and 206 cm^{-1}) almost quantitatively.

The present result clearly indicates that the metal-assisted peroxidation reaction (cf. eq 1) proceeds via organoperoxo complexes exemplified by **1** or **2**. This stepwise pathway for the formation of diorganoperoxides has been suggested previously.[3] However, the mechanistic details with respect to the initial attack of an organic electrophile such as alkyl- or acyl halide still remain to be elucidated. Questions may be raised regarding the transition state. Three distinct structures (I–III) shown below are conceivable for the bimolecular reaction.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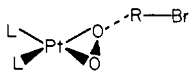
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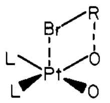
III

Transition-state I is rather unlikely if PtO_2L_2 retains the planar structure in which the axial *vacant* MO is not available in the frontier orbitals.[2a] However, if pyramidalization (Br–Pt–L, Br–Pt–O > 90°) occurs, the situation will change and such a transition state as I cannot readily be disregarded. Population analysis of $NiO_2(HNC)_2$ by semiempirical MO calculation at a level of MINDO approximation indicates[2a] that the net charges on the O_2 ligand and the metal are –0.88 and nearly zero, respectively. According to a recent CNDO MO calculation[2c] on $PtO_2(PH_3)_2$, the electronic charges of Pt and O_2 are +0.21 and –0.82, respectively. Thus the coordinated dioxygen in these complexes carries a negative charge close to superoxide ion. It seems then reasonable to postulate a S_N2-type transition state, II, or a cyclic transition state, III. An intermediate similar to II or III has been postulated in the reaction of ketones with $IrCl(O_2)(CO)(PPh_3)_2$[12] or $PtO_2(PPh_3)_2$,[6b,10b,c] respectively.

The diagnosis between these transition states should, in principle, be possible, employing an optically active alkyl halide. Transition-state structure I would result in loss of the stereochemical integrity at the chiral carbon, whereas II and III would lead to the inversion and retention, respectively. A secondary alkyl halide, α-phenethyl bromide, was chosen as the probe since the halide was found to react with $PtO_2(PPh_3)_2$, giving the desired product, an (alkylperoxo)metal complex. (*S*)-(–)-α-phenethyl bromide of 68% optical purity[24] was prepared[25] from (*R*)-(+)-α-phenethyl

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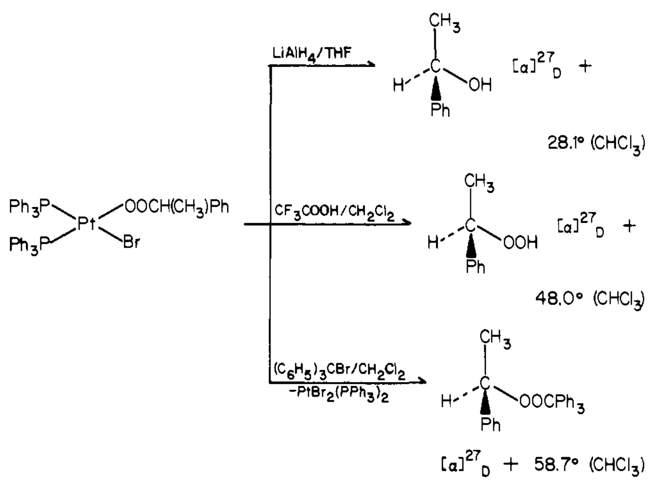
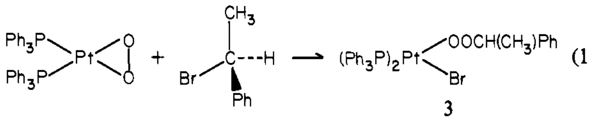
[24] The optical purity was calculated on the following values: $[\alpha]^{27}{}_D$ + 54.4° ($CHCl_3$) for (*R*)-(+)-α-phenetyl alcohol; $[\alpha]^{27}{}_D$ –111.5° ($CHCl_3$) for (*S*-(–)-α-phenethyl bromide. Lau, K. S. Y.; Wong, P. K.; Stille, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 5832–5840.

Scheme I



alcohol (92% optical purity). The reaction of this optically active bromide in CH_2Cl_2 gave a pale yellow peroxo complex, **3**, $[\alpha]^{27}_D$ +2.76. The IR spectrum (Nujol) shows weak bands at 840 and 920 cm^{-1}, the strong O–O stretching band (825 cm^{-1}) characteristic to $PtO_2(PPh_3)_2$ disappeared. The ^1H NMR (CD_2Cl_2) contained signals at δ 1.03 (d, CH_3) and 4.51 (q, CH). These spectral properties and analytical data are consistent with the formulation as an alkylperoxo compound, **3** (eq 11).



(11)

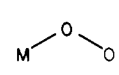
3

The absolute configuration at the chiral carbon of phenethyl group in **3** could readily be determined by releasing the corresponding alcohol, hydroperoxide, or dialkyl peroxide (Scheme I). Thus, the reductive cleavage of the oxygen–oxygen linkage can be effected with $LiAlH_4$ in THF. α-Phenethyl alcohol, isolated in 52% yield, shows an optical rotation ($[\alpha]^{27}_D$ +28.1°) corresponding to 51.7% optical purity.[24] The positive $[\alpha]_D$ value indicates *R* configuration at the carbon atom which is opposite of that for the starting compound (*S*)-(−)-α-phenethyl bromide. The optical yield is 76% for the process α-phenethyl bromide → **3** → α-phenethyl alcohol.

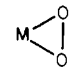
The metal–peroxo linkage of **3** can be cleaved by protolysis. Thus, careful hydrolysis of **3** with CF_3CO_2H produced (*R*)-(+)-α-phenethyl hydroperoxide[26] ($[\alpha]^{27}_D$ +48.9° ($CHCl_3$)) in 45.4% yield. The optical yield was not determined, as the optical rotation in $CHCl_3$ was not available.

Treating **3** with triphenylmethyl bromide, (*R*)-(+)-α-phenethyl triphenylmethyl peroxide[26a] ($[\alpha]^{27}_D$ +58.7° ($CHCl_3$)) and *cis*-$PtBr_2(PPh_3)_2$ were isolated in 54.5% and quantitative yield, respectively. The optical purity of the peroxide assessed from the reported maximum rotation[26b] was 58.7% corresponding to 86% optical yield. The stereochemical integrity of the benzylic carbon of complex **3** should remain intact in these cleavage reactions. Therefore it can safely be concluded that an inversion takes place during attack of the *sec*-alkyl halide on PtO_2L_2. Hence the S_N2-type transition-state II is more likely rather than I and III.

A question still remains as to whether the η^1-O_2 form is involved as we proposed previously (eq 2). This question has also been raised and discussed for the reaction of $IrCl(CO)L_2O_2$ with ketones, no definite answer being obtained. It may be pertinent to point out here that isotopic IR studies on $M(O_2)(t\text{-BuNC})_2$ (M = Ni, Pd) and $PtO_2(PPh_3)_2$ indicate[27] the dioxygen coordination in $PdO_2(t\text{-BuNC})_2$ to be unisosceles. This observation is consistent with the trend of O_2 dissociation from PdO_2L_2[28] where L is a bulky phosphine like $PPh(t\text{-Bu})_2$. Furthermore, there are both vacant and filled MOs of a_1 and b_1 symmetry in the frontier orbitals of MO_2L_2 complexes. It is therefore reasonable to conceive that the asymmetric vibration (b_1 mode) would lower the free energy of an asymmetric excited state, which facilitates deformation of the MO_2 moiety into an asymmetric η^2-coordination, a structure somewhere in between A and B. The electrophile would then prefer to attack on the distal oxygen atom carrying the increased electron density rather than on the proximal oxygen atom.



A



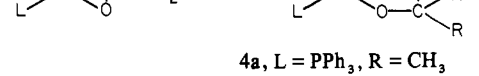
B

An interesting epoxidation of simple olefins was achieved by Kochi et al.[29] with a mixture of benzoyl chloride and $PtO_2(PPh_3)_2$. As the epoxidizing agent a peroxymetal complex similar to **2** was postulated but not isolated. Since we have the peroxo compound in hand, the reactivity toward olefins was tested. We observed a facile reaction of **2** with triphenylphosphine producing triphenylphosphine oxide and (benzoato)platinum complexes.

$$PtBr[OOC(O)Ph](PPh_3)_2 + PPh_3 \rightarrow Ph_3PO + PtBr[OC(O)Ph](PPh_3)_2 \quad (12)$$

The latter complex shows IR bands at 1634 (ν(CO)) and at 840 cm^{-1}. The low-frequency band, showing an isotopic shift to 827 cm^{-1} upon ^{18}O labeling, was not assigned. Complex **2** readily oxidizes norbornene, affording *exo*-norbornene epoxide[30] in 40% yield, a feature reminiscent of electrophilic peracids. The dramatic modification from the nucleophilic dioxygen ligand in PtO_2L_2 to the electrophilic peroxo complex is noteworthy. The capability of MOOC(O)R species to epoxidize an olefin may have implications for the active species involved in certain native oxygenases.

Reaction with Ketones. The reaction of PtO_2L_2 with ketones are known to give perketyl complexes. The molecular structure of the representative complex **4a** has been established by an X-ray analysis.[10a] ^{18}O isotopic IR studies were carried out on the perketyl complexes **4a,b** and **5a,b** prepared according to the known method.[11] As shown in Table I, the band at 811 cm^{-1} of **4a** assignable to the ^{16}O–^{16}O stretching band shifts to 786 cm^{-1} by substituting $^{16}O_2$ with 99% ^{18}O, and the ν(^{16}O–^{18}O) band can be observed at 793 cm^{-1} by employing $PtO_2(PPh_3)_2$ prepared with 23% ^{18}O. The ν(M–O) band at 379 cm^{-1} of **4a** shifts to 371 cm^{-1} on labeling with ^{18}O. Similar ^{18}O isotopic shifts are observed for both stretching regions of **4b** (Table I). These IR data indicate in support of reaction type 2 (eq 6) that the O–O moiety in perketyl complexes **4a** and **4b** is derived from the dioxygen ligand of PtO_2L_2.



(13)

4a, L = PPh_3, R = CH_3
b, L = $P(c\text{-}C_6H_{11})_3$, R = CH_3
5a, L = PPh_3, R = Ph
b, L = $P(c\text{-}C_6H_{11})_3$, R = Ph

This inference is further confirmed by the following IR study (Table II). Labeling with ^{18}O of **5a** was achieved in two ways: one from reaction of $Pt(^{18}O_2)(PPh_3)_2$ (99% ^{18}O) with Ph_2CO and the other from reaction of $PtO_2(PPh_3)_2$ with $Ph_2C^{18}O$.[31] Similarly, two types of labeled **5b** were prepared. **5b** prepared from Pt-

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[25] Hoffman, H. M. R.; Hughes, E. D. *J. Chem. Soc.* **1964**, 1244–1249.

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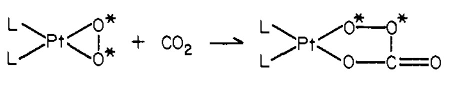
Table II. IR ^{18}O Isotope Shifts on IR Spectra of Perketyl Complexes (cm^{-1})

	compd	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
5a	$PtOOC(O)Ph_2(PPh_3)_1$	1056	780, 776	609	563	490	376
	$Pt^{18}O^{18}OC(O)Ph_2(PPh_3)_2$	1056	780, 758	608	540	479	365
	$PtOOC(^{18}O)Ph_2(PPh_3)_2$	1048	774	592	558	484	376
5b	$PtOOC(O)Ph_2[P(c\text{-}C_6H_{11})_3]_2$	1048	780	591	557	493	385
	$Pt^{18}O^{18}OC(O)Ph_2[P(c\text{-}C_6H_{11})_3]_2$	1050	767	588	544	483	376
	$PtOOC(^{18}O)Ph_2[P(c\text{-}C_6H_{11})_3]_2$	1043	773	575	550	491	385

$(^{18}O_2)[P(c\text{-}C_6H_{11})_3]_2$ and Ph_2CO shows four IR bands shifted from those (780, 557, 493, and 385 cm^{-1}) of the ^{16}O complex while **5b** prepared from $Pt(^{16}O_2)[P(c\text{-}C_6H_{11})_3]_2$ and $Ph_2C^{18}O$ shows two IR bands shifted from those (1048 and 591 cm^{-1}) of the ^{16}O complex. On the basis of our assignments of ν(O–O) and ν(M–O) for the perketyl complexes **4a** and **4b**, the bands at 780 and 385 cm^{-1} can be assigned to the ν(O–O) and ν(M–O) stretching modes, respectively. The bands at 1048 and 591 cm^{-1} observed for **5b** labeled with $Ph_2C^{18}O$ may be associated with the carbonyl group. Two peaks at 557 and 493 cm^{-1} may be associated with the vibrational modes of the moiety M–O–O–C, since these bands show larger isotopic shifts for the labeled **5b** made from $Pt(^{18}O_2)L_2$ than for the complex prepared from $Ph_2C^{18}O$.

It must be noted that the ν(O–O) band at 780 cm^{-1} appears to be mixed with the C-O vibration as a small isotopic shift from 780 to 774 cm^{-1} was detected in the complex prepared from PtO_2L_2 and $Ph_2C^{18}O$ (Table II). Similar isotopic bands were observed for the complex **5a** upon ^{18}O labeling. In this case, however, the 776-cm^{-1} band appears as a shoulder of the unassignable 780-cm^{-1} band.

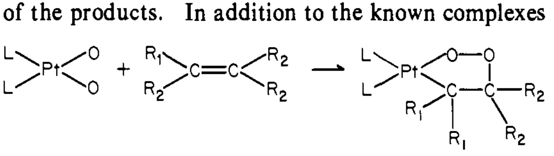
A peroxycarbonato complex (**6**)[32]


(14)

6, L = $P(c\text{-}C_6H_{11})_3$

prepared from $PtO_2[P(c\text{-}C_6H_{11})_3]_2$ and CO_2 shows an IR O–O stretching band at 822 cm^{-1} which shifts to 803 cm^{-1} in the complex prepared from $Pt(^{18}O_2)[P(c\text{-}C_6H_{11})_3]_2$ (99% ^{18}O). Again the original O–O linkage of dioxygen ligand retained in the peroxycarbonato complex, as is the case for the insertion reaction of ketones.

Reaction with Olefins and Acetylenes. The reactions of dioxygen complex $PtO_2(PPh_3)_2$ with electrophilic olefins $(CH_3)_2{=}C(CN)_2$ and $(NC)_2C{=}C(CN)_2$[22] were reinvestigated by isotopic IR studies of the products. In addition to the known complexes (**8a**, **9a**),


(15)

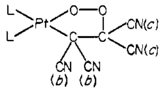
8a, L = PPh_3, R = CN, R_2 = CH_3
8b, L = $P(c\text{-}C_6H_{11})_3$, R_1 = CN, R_2 = CH_3
9a, L = PPh_3, R_1 = R_2 = CN
9b, L = $P(c\text{-}C_6H_{11})_3$, R_1 = R_2 = CN

we also prepared analogous complexes (**8b**, **9b**) from $PtO_2[P(c\text{-}C_6H_{11})_3]_2$. The ^{18}O labeling of **8a** was achieved by employing $PtO_2(PPh_3)_2$ labeled with 99% ^{18}O or 23% ^{18}O. Labeling **8b**, **9a**, and **9b** was done with 99% ^{18}O. Their distinct isotopic shifts observed are listed in Table I.

Table III. ^{13}C Chemical Shifts (ppm)[a]

	CN(PtCCN)[b]		CN(OCCN)[c]	
9a	114.31 114.05	J_{P-C} = 7.4 Hz	109.20	
9b	115.53 115.31	J_{P-C} = 5.9 Hz	109.26	
	CH_3	C=C	C=O	
10a	51.02	143.42	166.32	
10b	50.79	144.96	166.74	
	CN	C=*C*CN	H_3C*C*=C	CH_3
11	118.15	77.21	160.33	27.13

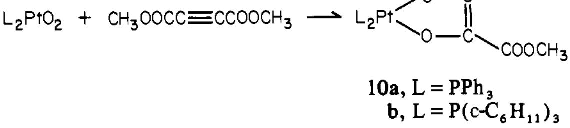
[a] Measured in $CDCl_3$ except 9a,b (CD_2Cl_2 was used). $CDCl_3$ was used as internal reference. [b,c] Showed the following CN carbons.



The ^{16}O complex **8a** shows bands at 813 and 371 cm^{-1}. The ^{16}O–^{18}O and ^{18}O–^{18}O bands can be observed at 798 and 775 cm^{-1}, respectively. The Pt–^{16}O band (371 cm^{-1}) shifts to 366 cm^{-1}. The complexes **8b**, **9a**, and **9b** labeled with 99% ^{18}O shows the respective ^{18}O–^{18}O and Pt–^{18}O band (Table I). Hence, we conclude that the complex **8a,b** and **9a,b** contains a peroxo linkage. As the ^{13}C NMR of **9a** and **9b** was not reported, we record these data in Table III. The observation of two inequivalent CN groups is consistent with the assigned structure. Although the ^{13}C resonances of $P(c\text{-}C_6H_{11})_3$ are complicated, comparison with those of the acetylenedicarboxylate adduct complex (**10b**), which contains two equivalent $P(c\text{-}C_6H_{11})_3$ ligands, allows us to conclude the presence of inequivalent $P(c\text{-}C_6H_{11})_3$ ligands in **9b**. Thus, as shown in Figure 1, in the **9b** spectrum there are two peaks corresponding to each one of peaks in the **10b** spectrum. Hence, the present spectroscopic studies unambiguously verify the structural assignment of these olefin adducts as **8a,b** and **9a,b**.

A similar reaction may be expected for the reaction of $PtO_2[P(c\text{-}C_6H_{11})_3]_2$ with dimethyl azodicarboxylate. Unexpectedly, however, the isolated compound was a (carbonato)platinum complex, **7**. As we have been unable to obtain information regarding the intermediate, the reaction mechanisms remain unknown.

All the reactions of PtO_2L_2 with such electrophiles as alkyl halide, ketone, and olefin we have examined so far involve asymmetric rupture of the metal–dioxygen bonds. Therefore, the reaction of $PtO_2[P(c\text{-}C_6H_{11})_3]_2$ with dimethyl acetylenedicarboxylate yielding a cyclic peroxide complex (eq 16) is indeed


(16)

10a, L = PPh_3
b, L = $P(c\text{-}C_6H_{11})_3$

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(31) Doering, W. von E.; Dorfman, E. *J. Am. Chem. Soc.* **1953**, *75*, 5595–5598.

(32) Two bands at 1680 and 780 cm^{-1} in IR spectra of peroxycarbonato complex, $PtOOC(O)O[P(c\text{-}C_6H_{11})_3]_2$ were assigned to ν(C=O) and ν(O–O), respectively, by Clark et al. Clark, H. C.; Goel, A. B.; Wong, C. S. *J. Organomet. Chem.* **1978**, *152*, C45–C47.

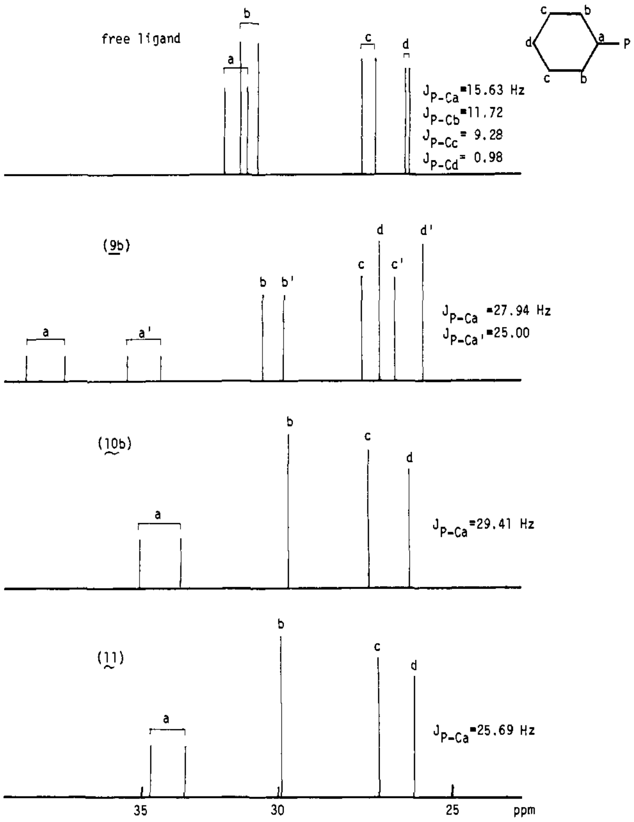
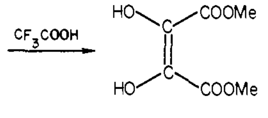


Figure 1. ^{13}C chemical shifts of cyclohexyl of phosphine ligand.

unique. The structure proposed for **10b** has been based on the single methyl proton resonance and a single ^{31}P resonance coupled with the IR data involving a strong C=C stretching band at 1580 cm^{-1}.[23] We measured ^{13}C NMR and ^{18}O isotoopic IR spectra of **10a** and **10b** (Tables I and III). The ^{13}C NMR shows three carbon signals, corresponding to the methyl, olefinic, and carbonyl carbon atoms, each being single signal consistent with the symmetrical cyclic structure. The ^{18}O-labeled 10a and 10b were prepared from dimethyl acetylenedicarboxylate and PtO_2L_2 (L = PPh_3, $P(c\text{-}C_6H_{11})_3$) containing 99% ^{18}O or 23% ^{18}O. The IR spectra of **10a** and **10b** do not contain bands in the region between 750 and 900 cm^{-1} which show an ^{18}O isotopic shift. Thus, the IR data, being consistent with the ^{13}C NMR, suggest the absence of an O–O bond. Isotopic bands associated with the M–O stretchings could not be found near 400 cm^{-1}. The ^{13}C NMR spectrum for the phosphine ligands also indicates a symmetrical structure as described above (Figure 1).

Complex **10b** was hydrolyzed with trifluoroacetic acid to give dimethyl dihydroxymaleate[33] in a good yield (eq 17), a result

10a  (17)

$$10a \xrightarrow{CF_3COOH} (HO)(MeOOC)C{=}C(OH)(COOMe) \quad (17)$$

consistent with structure **10b** proposed by Clark et al.[23] The present results, however, do not exclude the possibility of an initial formation of a metallocyclic peroxo species which subsequently rearranges to **10**.

On the basis of the kinetics and ^{31}P NMR showing two equivalent ^{31}P resonances a two-step reaction scheme was proposed. It order to detect the intermediate of the reaction (eq 16), we measured ^{13}C and ^{1}H NMR spectra of an equimolar mixture of PtO_2L_2 and the acetylene at -20 °C, at which temperature the reaction takes place slowly. Both spectra showed only resonances belonging to the starting compounds and the product. Again the result does not exclude involvement of a transient species.

The reaction with an unsymmetrically substituted acetylene $CH_3C{\equiv}CCN$[34] was then studied expecting that the polarized acetylene would stabilize the unsymmetrical adduct like **10**. The IR and NMR spectra of the yellow product **11** obtained from $PtO_2[P(c\text{-}C_6H_{11})_3]_2$ and $CH_3C{\equiv}CCN$ are shown in Tables I and III. The strong IR O–O stretching band at 825 cm^{-1} of PtO_2L_2 disappeared, and bands assignable to ν(C≡N) (2173 cm^{-1}) and ν(C=C) (1610, 1605 cm^{-1}) were observed. None of the IR bands between 700 and 950 cm^{-1} showed isotopic shifts when labeled PtO_2L_2 (99% ^{18}O) was used. The ν(M-O) near 400 cm^{-1} which appears in the spectrum of **9b** could not be found. The ^{13}C NMR spectra showed four different single signals assignable to two types of olefinic carbons, one methyl carbon and one cyano carbon. These signals did not show any appreciable coupling with ^{195}Pt or with ^{31}P. As Figure 1 shows, the ^{13}C spectrum of cyclohexyl carbons of phosphine ligands of **11** is very similar to that of **10b** which has a symmetrical structure. These IR and NMR studies thus suggest the absence of the O–O bond in complex **11**. Although the available data are in support of a structure analogous to **10**, a conclusive structural assignment of **11** requires further studies.

Attempts for protolysis of **11** with trifluoroacetic acid do not give the expected olefinic glycol, untractable substances being formed. The mechanism of the reaction of acetylenes with dioxygen complexes still remains to be elucidated.

Experimental Section

All manipulations and reactions involving metal complexes were carried out under a pure dinitrogen atmosphere. Infrared spectra were recorded on a Hitachi Perkin-Elmer Model 225 spectrometer. The ^{13}C NMR spectra were obtained on a JNM FX100 Fourier transform spectrometer.

Starting materials, $PtO_2(Ph_3P)_2$,[35] and $PtO_2[P(c\text{-}C_6H_{11})_3]_2$[28] were prepared by known methods. Reactions of $(Ph_3P)_2PtO_2$ with acetone and olefins and subsequent isolation of the products were performed according to published procedures.[11,22] Isotopically labeled $^{18}O_2$ (99% and 23%) was obtained from BOC Limited Prochem. Analytical data of all the new compounds were in good agreement with the calculated values.

Preparation of $PtBr(OOCPh_3)(PPh_3)_2 \cdot CH_2Cl_2$ (1a). To a solution of $PtO_2(PPh_3)_2 \cdot C_6H_6$ (0.666 g, 0.803 mmol) in methylene chloride (7 mL) was added solid triphenylmethyl bromide (0.262 g, 0.811 mmol) at -78 °C under stirring. The initial yellow color of the solution faded into pale yellow. During stirring for 1 h, the solution gradually became turbid. Hexane (18 mL) being added, the temperature of the mixture was allowed to reach -20 °C. The fine pale-yellow crystals formed were filtered, washed with cold hexane (20 mL) twice at -20 °C, and dried in vacuo. They were analytically pure. As revealed by the elemental analysis, 1 mol of methylene chloride was involved as the crystallization solvent. The yield was 0.723 g (0.623 mmol, 78%), mp 143-144 °C dec. The molecular weight measured by vapor pressure osmometry was 1020 in methylene chloride but 630 in benzene (calcd 1074).

Similarly, the reaction of $PtO_2[P(c\text{-}C_6H_{11})_3]_2$ with 1 mol of triphenylmethyl bromide was carried out in methylene chloride to give the complex $PtBr(OOCPh_3)[P(c\text{-}C_6H_{11})_3]_2$ (**1b**) as pale yellow crystals (82% yield), mp 138-1340 °C dec. Almost complete removal of methylene chloride was necessary to isolate the product because of its enhanced solubility.

Reaction of 1a with Triphenylmethyl Bromide. To a suspension of **1a** (0.312 g, 0.269 mmol) in a mixture of methylene chloride (20 mL) and toluene (20 mL) was added solid triphenylmethyl bromide (0.105 g, 0.325 mmol) at room temperature. The mixture was stirred at 50 °C for 2 h and the stirring continued overnight at room temperature. After the resultant yellow solution was concentrated to ca. 10 mL, toluene (20 mL) was added. The off-white powder that precipitated was collected by filtration and recrystallized from a methylene chloride–hexane mixture. This was readily identified as the known bromide *cis*-$PtBr_2(PPh_3)_2$ (0.186 g, 78.6%), mp 310 (IR ν(Pt-Br) 219 and 206 cm^{-1}). The filtrate was concentrated to dryness. The residue was washed with ether (20 mL) several times to remove unreacted triphenylmethyl bromide and recrystallized from CS_2 to give bis(triphenylmethyl) peroxide as white crystals (0.093 g, 67%), mp 185 °C (lit.[36] 185-186 °C).

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[33] Fenton, H. J. H. *J. Chem. Soc.* **1894**, *65*, 899-910.

[34] Benes, M. J.; Peska, J.; Wichterie, O. *J. Polym. Sci., Part C* **1967**, *16*, 555-560.

[35] (a) Takahashi, S.; Sonogashira, K.; Hagihara, N. *Nippon Kagaku Zasshi.* **1966**, *87*, 610-613. (b) Cook, C. D.; Jauhal, G. S. *J. Am. Chem. Soc.* **1968**, *90*, 1464-1467.

Similar reaction of **1b** with triphenylmethyl bromide gave the peroxide in 60% yield.

Preparation of $\mathbf{PtBr[OOC(O)Ph](PPh_3)_2}$ (2). To a solution of $PtO_2(PPh_3)_2{\cdot}C_6H_6$ (0.319 g, 0.385 mmol) in methylene chloride (7 mL) was added a solution of benzoyl bromide in hexane (0.80 mL, 0.48 M) at −78 °C under stirring. The initial yellow color disappeared immediately. The temperature was allowed to reach −40 °C. Hexane (20 mL) being added dropwise to the mixture at −40 °C, the product precipitated as white microcrystals. The solid was separated by filtration from the reaction mixture chilled below −70 °C, washed with cold hexane, and dried in vacuo; the yield was 0.283 g (0.302 mmol, 79%), mp 129–130 °C dec. A careless rapid addition of a large portion of the poor solvent hexane resulted in an untractable oily material.

Reaction of 2 with Benzoyl Bromide. To a solution of the complex **2** (0.208 g, 0.222 mol) in methylene chloride was added slowly a solution of benzoyl bromide in hexane (0.52 mL, 0.48 M, 0.250 mmol) at −78 °C. After stirring for 6 h at −78 °C, the reaction mixture was kept overnight in a refrigerator (below 5 °C). Ether (50 mL) being added, the mixture was allowed to stand at room temperature to give a pale brown precipitate. The mixture was filtered, and recrystallization of the solid product from a methylene chloride–hexane mixture gave *cis*-$PtBr_2(PPh_3)_2$ (78% yield). Evaporation of the filtrate gave a brown tarry product. This was dissolved in ether, and the ether solution was treated with 0.1 N NaOH to remove unreacted benzoyl bromide. After being dried over anhydrous Na_2SO_4, the organic layer was subjected to a thin-layer chromatography (silica gel). Two major spots obtained were found to be benzoyl peroxide (0.116 g, 22%) and benzoic anhydride (0.0134 g, 27%) by comparing their IR spectra and melting point with those of the authentic samples.

Reaction of 2 with Triphenylphosphine. The mixture of complex **2** (0.054 g, 0.058 mmol) and triphenylphosphine (0.017 g, 0.064 mmol) in methylene chloride (3 mL) was stirred at −78 °C for 1 h. After the reaction mixture was concentrated to ca. 1 mL, ether (15 mL) was added to give an off-white powder, mp 226 °C, which was characterized as bromo(benzoato)bis(triphenylphosphine)platinum(II) by elemental analysis and the IR spectra (72% yield). The IR spectra showed a strong band at 1634 cm^{-1} assignable to ν(CO). From the ether solution, triphenylphosphine oxide was obtained in quantitative yield.

Preparation of $\mathbf{PtBr[OOCH(CH_3)Ph](PPh_3)_2{\cdot}CH_2Cl_2}$ (3). To a solution of $PtO_2(PPh_3)_2\ C_6H_6$ (0.654 g, 0.789 mmol) in methylene chloride (15 mL) was added 0.146 g (0.789 mmol) of optically active α-phenethyl bromide,[25] $[\alpha]^{27}{}_D$ −75.7° (*c* 3.42, $CHCl_3$, *l* = 0.5, 68% optically pure[24]) at −40 °C while being stirred. The temperature of the mixture was allowed to reach ambient temperature. After being stirred overnight at the temperature, the yellow solution was poured into a 70 mL of hexane and concentrated to ca. 10 mL by removing methylene chloride, followed by addition of hexane (70 mL) to give a pale yellow powder. This was washed with hexane twice and dried in vacuo. The yield was 0.579 g (0.566 mmol, 72%), mp 134–136 °C dec. The product was analytical pure and shown to have an optical activity: $[\alpha]^{27}{}_D$ +27.6° (*c* 2.03, $CHCl_3$, *l* = 1.0).

Similar reaction of $PtO_2[P(c\text{-}C_6H_{11})_3]_2$ with 1-phenethyl bromide gave unidentifiable oily substances.

Reaction of 3 with Lithium Aluminium Hydride. To a solution of **3** (0.643 g, 0.630 mmol) in THF (20 mL) was slowly added solid $LiAlH_4$ (0.080 g, 2.056 mmol) at 0 °C under stirring. With evolution of hydrogen gas, the initial yellow solution turned to dark brown. After being heated at 60 °C for 20 min, the mixture was concentrated to dryness and the residue was dissolved in ether. For decomposing of the excess of $LiAlH_4$, water was added and the mixture acidified with diluted H_2SO_4. The aqueous layer was washed with ether several times. The ether extract and washings were combined and dried over Na_2SO_4. After all solvents were removed, the residual oil was distilled at 80–100 °C (10mmHg) to give an colorless oil (40 mg, 52%) which was identified as α-phenethyl alcohol by comparing the IR and ^{1}H NMR spectra with those of the authentic sample. The optical purity of the product was 52%,[24] $[\alpha]^{27}{}_D$ + 28.1 (*c* 0.438 $CHCl_3$, *l* = 1.0).

Reaction of 3 with Trifluoroacetic Acid. To a solution of **3** (0.619 g, 0.606 mmol) in methylene chloride (15 mL) was added trifluoroacetic acid (0.077 g, 0.674 mmol) dropwise at −20 °C. The temperature of the mixture was allowed to rise to ambient temperature. An initial pale yellow color turned to deep yellow. After being stirred for 3 h at the temperature given above, the mixture was evaporated to dryness and the residue was extracted with ether. The ether extract was washed with saturated aqueous sodium hydrogen carbonate and subsequently with water and dried (Na_2SO_4). Removal of the ether gave an pale yellow oil which was distilled, yielding 1-phenylethyl hydroperoxide[26] (38 mg, 45.4%), bp 40–60 °C (0.3mmHg); IR (neat) 3375 cm^{-1} (ν(O–H)) 842 cm^{-1} (ν(O–O)); NMR (CCl_4) δ 1.41 (d, 3 H, *J* = 6.8 Hz, $-CH_3$), 2.42 (s, 1 H, −OH) 4.84 (q, 1 H, *J* = 6.4 Hz, −CH), 7.12 (m, 5 H, $-C_6H_5$); $[\alpha]^{27}{}_D$ +48.9° (*c* 0.305, $CHCl_3$, *l* = 1.0).

Reaction of 3 with Triphenylmethyl Bromide. To a solution of **3** (0.509 g, 0.498 mmol) in methylene chloride (15 mL) was added solid triphenylmethyl bromide (0.178 g, 0.551 mmol) at −40 °C under stirring. The initial yellow solution became turbid on stirring for 12 h at ambient temperature. Addition of 100 mL of ethanol to the reaction mixture gave quantitatively an yellow powder, *cis*-$PtBr_2(PPh_3)_2$. The filtrate was concentrated under vacuum, yielding an oily material from which colorless crystals (0.064 g, 0.246 mmol), mp 151 °C, were obtained on addition of hexane. The crystals were readily identified as triphenylcarbinol. The hexane solution was concentrated, yielding an oil which was subjected to preparative TLC of silica gel by using chloroform as the eluant. From the upper layer, an optically active 1-phenylethyl triphenylmethyl peroxide[26a] was obtained as a colorless oil (0.103 g, 55%): IR no ν(O–H), 798 cm^{-1} (ν(O–O)); NMR (CCl_4) δ 1.18 (d, 3 H, *J* = 7 Hz, $-CH_3$), 4.46 (q, 1 H, *J* = 7.2 Hz, −CH), 7.2 (m, 20 H, $-C_6H_5$); mass spectrum, parent ion at *m/e* 380; $[\alpha]^{27}{}_D$ +58.7° (*c* 0.765, $CHCl_3$, *l* = 1.0) (optical purity ca. 59%).[26b]

Preparation of $\mathbf{\overline{PtOOC(O)}(CH_3)_2[P(c\text{-}C_6H_{11})_3]_2}$ (4b). To a suspension of $PtO_2[P(c\text{-}C_6H_{11})_3]_2$ (0.150 g, 0.190 mmol) in hexane (50 mL) was added a large excess of acetone (10 mL) at room temperature under stirring. The initial suspension became a pale yellow clear solution and then a colorless solution. After being stirred for 2 h, the reaction mixture was concentrated to give an off-white powder (0.129 g, 80%), mp 138–140 °C.

Preparation of $\mathbf{\overline{PtOOC(O)}Ph_2(PPh_3)_2}$ (5a). To a suspension of $PtO_2(PPh_3)_2{\cdot}C_6H_6$ (0.200 g, 0.241 mmol) in benzene (4 mL) was added solid benzophenone (0.401 g, 2.2 mmol) at room temperature under stirring. Stirring was continued for 10 h until a clear solution was resulted. Ether (30 mL) was then added to the reaction mixture to give white crystals (0.185 g, 0.198 mmol, 82%), mp 165 °C dec.

Similarly, the reaction of $PtO_2[P(c\text{-}C_6H_{11})_3]_2$ with 2 mol of benzophenone in benzene gave the complex $\overline{\mathrm{PtOOC(O)}}\mathrm{Ph_2[P(c\text{-}C_6H_{11})_3]_2}$ (**5b**) as white crystals (80% yield), mp 180–181 °C.

Preparation of $\mathbf{\overline{PtOOC(O)O}[P(c\text{-}C_6H_{11})_3]_2}$[32] (6). To a solution of $PtO_2[P(c\text{-}C_6H_{11})_3]_2$ (0.188 g, 0.238 mmol) in toluene (10 mL) was introduced gaseous carbon dioxide. Colorless crystals appeared in the solution, the initial yellow color being faded. Hexane (30 mL) was then added to the mixture to give a colorless crystal (0.170 g, 86%), mp 137–140 °C.

Reaction of $\mathbf{PtO_2[P(c\text{-}C_6H_{11})_3]_2}$ with Dimethyl Azodicarboxylate. To a solution of $PtO_2[P(c\text{-}C_6H_{11})_3]_2$ (0.395 g, 0.502 mmol) in methylene chloride (12 mL) was added dimethyl azodicarboxylate (0.120 g, 0.821 mmol) at −40 °C under stirring. The red color of azo compound faded out very rapidly even at −40 °C. The temperature was allowed to reach ambient temperature, and the mixture was stirred overnight at the temperature. The mixture was poured into hexane (50 mL) and concentrated to dryness. For removal of an excess of the azo compound, the residue was washed with ether (10 mL) twice. The resulting pale yellow powder was recrystallized from toluene–hexane to give $\overline{\mathrm{PtOC(O)O}}\mathrm{[P(c\text{-}C_6H_{11})_3]_2}$ (**7**) as off-white crystals (0.168 g, 41%), mp 162–167 °C dec.

Preparation of $\mathbf{\overline{PtOOC(CH_3)_2C}(CN)_2[P(c\text{-}C_6H_{11})_3]_2}$ (8b) and $\mathbf{\overline{PtOOC(CN)_2C}(CN)_2[P(c\text{-}C_6H_{11})_3]_2}$ (9b). These complexes were prepared in the same way as employed for $\overline{\mathrm{PtOOC(CH_3)_2C}}\mathrm{(CN)_2(PPh_3)_2}$ and $\overline{\mathrm{PtOOC(CN)_2C}}\mathrm{(CN)_2(PPh_3)_2}$. The yields for **8b** and **9b** were 96% and 88%, respectively (mp 118–120 °C for **8b** and 132–134° for **9b**).

Preparation of $\mathbf{\overline{PtO(CH_3OOC)C{=}CO}(COOCH_3)(PPh_3)_2{\cdot}CH_2Cl_2}$ (10a). To a solution of $PtO_2(PPh_3)_2{\cdot}C_6H_6$ (0.312 g, 0.376 mmol) in methylene chloride (10 mL) was added dimethyl acetylenedicarboxylate (0.053 g, 0.376 mmol) at −40 °C under stirring. Stirring was continued for 1 h at −40 to −20 °C, for 2 h at −20 to +10 °C, and for 2 h at room temperature. The initial pale yellow solution turned to orange yellow. The mixture was poured into hexane (100 mL) to give an orange yellow powder (0.260 g, 71%), mp 135 °C dec.

Preparation of $\mathbf{\overline{PtO(CH_3OOC)C{=}CO}(COOCH_3)[P(c\text{-}C_6H_{11})_3]_2}$ (10b). To a solution of $PtO_2[P(c\text{-}C_6H_{11})_3]_2$ (0.273 g, 0.346 mmol) in methylene chloride was added dimethyl acetylenedicarboxylate (0.049 g, 0.346 mmol) at −40 °C under stirring. The reaction mixture was stirred at −40 to −20 °C for 1 h, and the temperature of the mixture was allowed to reach room temperature. After being stirred for 2 h, the mixture was then poured into hexane (130 mL). Concentration of the mixture gave a pale yellow powder (0.274 g, 85%), mp 180–182 °C dec.

Protrolysis of 10b with Trifluoroacetic Acid. To a solution of **10b** (0.506 g, 0.544 mmol) in methylene chloride (20 mL) was added tri-

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fluoroacetic acid (0.124 g, 1.088 mmol) at −40 °C. The temperature of the stirring mixture was allowed to rise to room temperature, and stirring was continued for 1 h. Hexane (50 mL) being added, the mixture was concentrated to dryness. The residue was washed with hexane to remove the unreacted acid, leaving a pale brown powder from which a white powder was sublimed at 110–140 °C (5mmHg). This was identified as dimethyl dihydroxymaleate by compairing the IR and ^{1}H NMR spectra and melting point with those of the authentic sample;[33] mp 150 °C (sublimed) lit. above 150 °C (sublimed). The yield was 0.065 (68%).

The hydrolysis of **10b** in methylene chloride with dry HCl or reduction with $NaBH_4$ in ethanol gave no identifiable product.

Reaction of $PtO_2[P(c\text{-}C_6H_{11})_3]_2$ with $CH_3C{\equiv}CCN$. To a solution of $PtO_2[P(c\text{-}C_6H_{11})_3]_2$ (0.376 g, 0.477 mmol) in methylene chloride was added 1-cyanopropyne[34] (0.034 g, 0.518 mmol) at −40 °C under stirring. The temperature was allowed to reach 0 °C and stirring was continued at 0 °C for 1.5 h. The initial pale yellow turned to light orange. After being stirred for 5 h at ambient temperature, the solution was poured into hexane (80 mL) to yield a yellow powder **11** which was filtered off, washed with hexane (10 mL) three times and dried in vacuo. The yield was 0.299 g (0.351 mmol, 73%), mp 166–168 °C dec. **11** was characterized by elemental analysis, IR, and ^{1}H and ^{13}C NMR spectroscopies. The results are consistent with a formula as $\overline{PtO(CH_3)C{=}CO}(CN)$-$[P(c\text{-}C_6H_{11})_3]$ similar to **10** (see text).

Similar reaction of $PtO_2(PPh_3)_2$ with 1-cyanopropyne in methylene chloride gave an yellow powder whose IR spectrum and elemental analysis confirmed a cyclic adduct analogous to **11**.

Attempts to hydrolyze **11** with trifluoroacetic acid gave the platinum(II) complex $Pt(OCOCF_3)_2[P(c\text{-}C_6H_{11})_3]_2$ and a mixture of red oily untractable substances.

Activation Barriers for Heterogeneous and Homogeneous Electron Transfer. Experimental Tests for Marcus Theory in the Oxidation of Organometallic Complexes

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Abstract: Electron transfer is carried out both chemically and electrochemically from four structurally diverse classes of organometallic complexes including those with octahedral, square-planar, tetrahedral, and linear structures. The activation free energies $\Delta G_h^{\ddagger}$ and $\Delta G_e^{\ddagger}$ for the homogeneous and heterogeneous rate processes, respectively, are linearly correlated, provided they are evaluated at the same thermodynamic driving force (i.e., potential). Indeed, the slope of the correlation (Figure 7) is precisely unity when the quadratic Marcus equation describes the free-energy relationship required to span the potential gap between the homogeneous and the heterogeneous rate data. The concordance of the homogeneous and heterogeneous rate processes for organometals is also shown (Figure 9) by the direct correlation of the potential dependences of $\Delta G_h^{\ddagger}$ and $\Delta G_e^{\ddagger}$, as given by the Brønsted coefficient α and the transfer coefficient β, respectively. The observation of second-order effects, as slight curvatures in the potential dependences of α and β (i.e., $\partial\alpha/\partial\Delta G_h$ and $\partial\beta/\partial\Delta G_e$), provides a further, critical test of the Marcus theory.

Introduction

Activation barriers for electron transfer are well provided for by the Marcus theory, particularly as it applies to outer-sphere processes.[1] Heretofore most of the studies of electron transfer have been carried out homogeneously with the chemical oxidants and reductants both in solution. Although there exist some electrochemical comparisons of heterogeneous electron-transfer processes, there are only a limited number of examples in which electron-transfer theories have enabled the clean correlation of the electrochemistry with the chemical rates.[2]

To achieve a direct comparison of the activation barriers for homogeneous and heterogeneous processes, at least two important experimental conditions must be met. First, the chemical oxidants (or reductants) must possess well-defined structural and electron-acceptor (donor) characteristics, and they must be kinetically and electrochemically well behaved. Second, methods must be readily available for the measurements of their heterogeneous electron-transfer rates at various applied potentials. Indeed, we recently showed that the chemical and the anodic oxidations of a homologous series of alkylmetals of tin, lead, and mercury fulfil these requirements.[3] Coupled with the studies of alkylplatinum complexes and organocobalt macrocycles,[4] we now have at our disposal a prescribed series of four structurally diverse classes of organometals, in which the configuration and the coordination about the metal vary systematically from octahedral, square planar, tetrahedral, to linear, as illustrated (I–IV). Each of these organometallic complexes is substitution stable, sufficient to allow meaningful kinetic and electrochemical measurements to be made.

Results

In the following oxidations, we have compared the electrochemical and chemical rate measurements at 25 °C in degassed acetonitrile as the common solvent, and in the presence of tetraethylammonium perchlorate (TEAP) to maintain constant ionic strength or to serve as the supporting electrolyte.

I. Kinetics of the Heterogeneous Oxidation of Organometals at the Platinum Electrode.

Anodic oxidation of the organometals

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