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A Laser Flash Photolysis Study of Transient Bis(triphenylphosphine)platinum(0)

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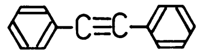
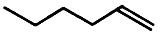
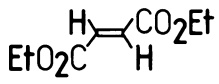
Transient spectra were obtained for bis(triphenylphosphine)platinum(0) (ε_{410}: 630 dm^{3}mol^{-1}cm^{-1}), to which O_2 and diphenyacetylene coordinated with second-order rate constants of 2.4×10^4 and 1.2×10^6 dm^{3}mol^{-1}s^{-1} respectively.

Zerovalent platinum complexes carrying large cone angle phosphines$^{1)}$ like $P(t\text{-}Bu)_3$ were isolated as inert two coordinate complexes by Otsuka et al.$^{2)}$ In the case of PPh_3, although $Pt(PPh_3)_2$ was supposed as a reaction intermediate$^{3)}$ or even reported to be isolated as an elusive species,$^{4)}$ only poor physical profile is available in the literature: Low-temperature matrices emitted blue light.$^{5)}$ We report here the absorption spectrum and dynamic properties of $Pt(PPh_3)_2$ in solution.

Figure 1(A) shows a typical reaction trace at 350 nm obtained by laser flash photolysis of bis(triphenylphosphine)dioxygenplatinum(0), $Pt(PPh_3)_2O_2$, in benzene under oxygen, which obeyed pseudo-first order reaction kinetics ($k_1'=k_2[O_2]$). Similar decays were observed also at other wavelengths; namely, the transient reacts with molecular oxygen to regenerate $Pt(PPh_3)_2O_2$.$^{5)}$ Transient spectrum shown in Fig. 1(C) was identical with those in toluene and fluorobenzene, and k_2 for O_2 was determined as an identical value in these three solvents (Table 1), indicating $Pt(PPh_3)_2$ being not coordinated by a solvent molecule.$^{6)}$ Since the absorbance of $Pt(PPh_3)_2O_2$ was very small at 410 nm, ε_{410} was estimated as 630 dm^{3}mol^{-1}cm^{-1} by assuming that the second order decay (k_2/ε_{410}) under argon was due to the recombination of $Pt(PPh_3)_2$ and O_2.$^{7)}$

Continuous irradiation of the dioxygen complex in the presence of diphenylacetylene with a 366 nm line of a mercury lamp gave bis(triphenylphosphine)(diphenylacetylene)platinum(0) (ϕ = 0.1), in accordance with the effective quenching of the 410 nm peak by diphenylacetylene as shown in Table 1. Compounds with electron-withdrawing groups seem to have larger rate constants of the coordination. The exception of molecular oxygen from this trend may be explained by its triplet ground state. On the other hand, although excited singlet molecular oxygen was reported to be generated on the photolysis of $Pt(PPh_3)_2O_2$ 5) and have a long lifetime in benzene (≈30 µs), 8) the reaction of singlet oxygen with $Pt(PPh_3)_2$ could not be observed even with a time-resolution of 20 ns/division as far as monitoring $Pt(PPh_3)_2$. This means that the reaction completed within the duration of the laser pulse, or that the yield of singlet oxygen on the photolysis was not high. Work on these points is in progress.

Table 1. Second-order rate constants ($dm^3 mol^{-1} s^{-1}$) for coordination to $Pt(PPh_3)_2$ at 20 °C obtained by the treatment of pseudo-first order reaction kinetics with varying concentrations of compounds at 410 nm

	O_2		$MeO_2C\text{-}C{\equiv}C\text{-}CO_2Me$		
k_2	2.3×10^4	1.2×10^6	5.2×10^7	2.6×10^6	1.9×10^7

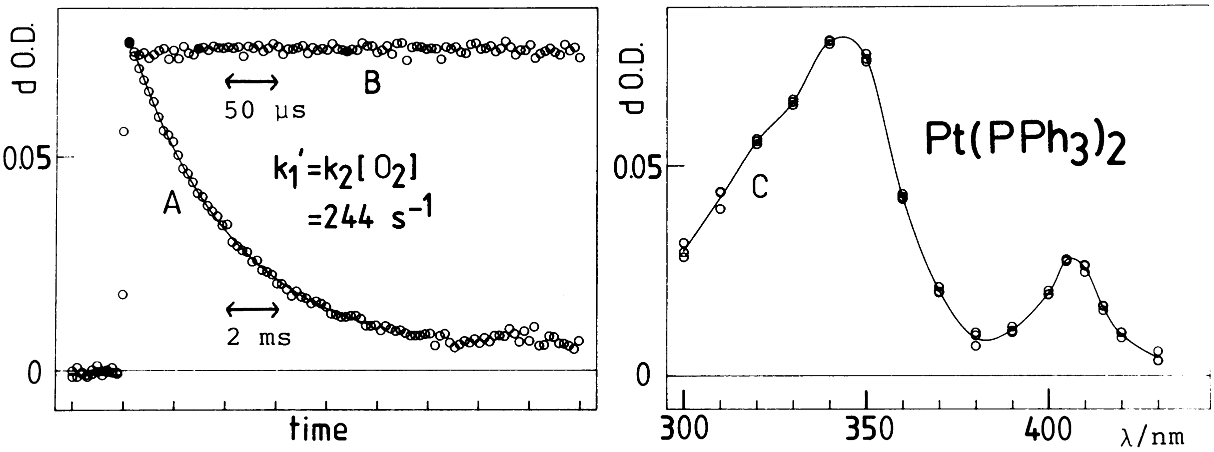


Fig.1.(A) $Pt(PPh_3)_2O_2$ in benzene (0.60 mM) was photolyzed under oxygen at an ambient temperature (20 °C) by a third harmonic (355 nm, 4 mJ/pulse, 7 ns of pulse width) from a Q-swiched Nd:YAG laser (Quanta-Ray DCR-11 modified to a stable resonator) and analyzed at 350 nm with a time scale of 2 ms/division. (B) A typical trace under air at 350 nm with 50 µs/division, from which solid circles were collected for composing Spectrum (C).

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