

References and Notes

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Received September 16, 1974

Mechanistic Studies of Oxidative Addition to Low Valent Metal Complexes. IV. Observation of CIDNP Effects in Platinum(0) and Palladium(0) Reactions

Sir:

In a previous communication¹ we offered evidence that the reactions of many alkyl (and related) bromides with $M(\text{PEt}_3)_3$ (**1**) ($M = \text{Pt}$, **1a**;² $M = \text{Pd}$, **1b**³) involve radical chain processes. In the scheme presented, the adduct *trans*- $\text{MRBr}(\text{PEt}_3)_2$ (**2**) and *trans*- $\text{MHBr}(\text{PEt}_3)_2$ (**3**) are both formed early in the reaction sequence, whereas *trans*- $\text{MBr}_2(\text{PEt}_3)_2$ (**4**) is produced in a slower, subsequent step involving **3** as an intermediate. We find, however, that several very reactive halides (e.g., α -bromoesters, benzyl bromide, secondary alkyl iodides) when allowed to react with **1** produce **4** too rapidly for the previously described chain process to be operative in these cases.⁴ The results presented here on the investigation of such reactions show other paths are indeed available and also provide the first definitive⁵ evidence that one-electron processes can be involved in these reactions.

When **1a** (1 mol) and isopropyl iodide (2.5 mol) are allowed to react in benzene- d_6 and/or toluene- d_8 at ambient temperatures, the reaction is complete within a few minutes, and analysis⁸ of the products shows *trans*- $\text{PtHI}(\text{PEt}_3)_2$ (0.45 mol), *trans*- $\text{PtI}_2(\text{PEt}_3)_2$ (0.55 mol), *trans*- $\text{Pt}(i\text{Pr})\text{I}(\text{PEt}_3)_2$ (trace), propene (0.75 mol), propane (0.30 mol), and 2,3-dimethylbutane (0.25 mol). When this reaction is followed by ¹H nmr spectroscopy, pronounced CIDNP enhancements (multiplet effects) are observed in the resonances of propene and isopropyl iodide.⁹ Identical observations were made for the reaction of isopropyl iodide

Scheme I

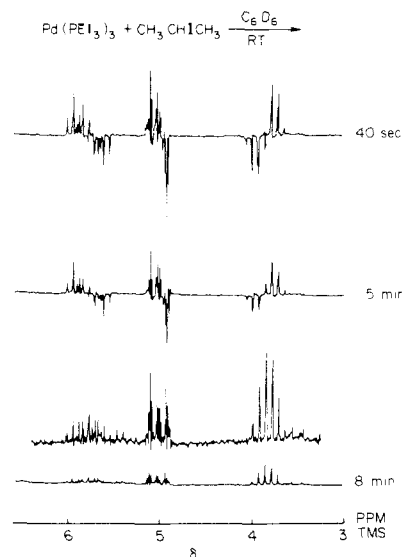
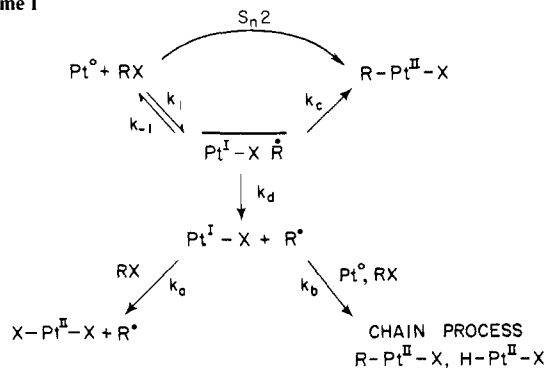


Figure 1. ¹H nmr spectra recorded at 100 MHz during the ambient temperature reaction of isopropyl iodide and $\text{Pd}(\text{PEt}_3)_3$ in benzene- d_6 .

with **1b** (Figure 1). These observations clearly indicate that at least a component of the reaction involves a radical (one-electron) process. The phase of the multiplet effects¹⁰ indicates that the predominant path for enhancement in both propene and isopropyl iodide involves the diffusive encounter of isopropyl radicals. Further evidence that this is a significant reaction path is provided by product analysis. When correction is made for propene produced by the competitive radical chain process (which is equal to the moles of *trans*- $\text{PtHI}(\text{PEt}_3)_2$ produced), the mole ratios of propene:propane:2,3-dimethylbutane (i.e., 0.30:0.30:0.25) are consistent with that expected for a disproportionation-combination reaction of isopropyl radical pairs.¹¹

The reaction of benzyl bromide (2.5 mol) and **1a** (1 mol) yields **2a** (0.2 mol), **4a** (0.8 mol), and bibenzyl (0.8 mol), the rate of addition and the product ratios being unaffected by the addition of 5 mol % duroquinone. During the reaction, CIDNP (multiplet) effects are observed in the aromatic resonances (¹H nmr), and, although the origin of these effects has yet to be determined, benzyl radicals are clearly implicated. However, in the reaction of **1a** with α -bromoethylbenzene, the AE multiplet effects observed in the nonaromatic resonances (¹H nmr) of the disproportionation products, ethylbenzene and styrene, characterize this process as one involving the diffusive encounter of α -methylbenzyl radicals.

It must be noted that we have observed CIDNP effects only when *trans*- $\text{MX}_2(\text{PEt}_3)_2$ ($X = \text{Br}, \text{I}$) is produced rapidly in the initial stages of the reaction, but, as yet, not in cases when only the regular addition and hydrido complexes, *trans*- $\text{MRX}(\text{PEt}_3)_2$ and *trans*- $\text{MHX}(\text{PEt}_3)_2$, are formed.¹² For example, benzyl chloride reacts cleanly with **1a** to yield the regular adduct, *trans*- $\text{Pt}(\text{CH}_2\text{C}_6\text{H}_5)\text{Cl}(\text{PEt}_3)_2$, in quantitative yield. No CIDNP effects are observed, in contrast to the corresponding reaction with benzyl bromide.

We have written a generalized scheme for alkyl halide reactions with **1**, drawing together these and other results (Scheme I). Platinum(0) may react initially with an organic halide by two paths.¹³ (i) One path is the $\text{S}_{\text{N}}2$ displacement on carbon to give an incipient cationic complex (possibly strongly ion paired) followed by reentry of the anion to give the regular oxidative addition adduct. Recent work by Stille^{7,14} strongly substantiates the feasibility of this route. (ii) The other path is halide abstraction (possibly preceded

by electron transfer) to form a radical pair ($\text{Pt}^1\text{-X} + \text{R}\cdot$). This pair can either collapse to the regular adduct⁶ or diffusively separate to form $\text{Pt}^1\text{-X}$ and $\text{R}\cdot$. Depending on the reactivity of the reactant alkyl halide, two pathways may then develop. For very reactive halides (as are described in this communication), $\text{Pt}^1\text{-X}$ can rapidly abstract further halide to yield dihalide and organic radical. CIDNP effects result from the diffusive encounter of these product radicals. Alternatively, for less reactive halides, the organic radical will initiate a chain process to produce regular adduct (and/or hydrido complex).

In the reaction of isopropyl iodide with **1a**, the chain process (k_b) to form hydrido complex and the abstraction process (k_a) to form diiodo complex are competitive. For isopropyl bromide, however, the chain mechanism dominates,¹ as might be expected since in terms of bond strength, $\text{C-Br} \gg \text{C-I}$.

Regular adduct formation in the reaction of benzyl bromide with **1a** could arise in two possible ways: (a) *via* the $\text{S}_{\text{N}}2$ process and (b) by radical pair collapse (k_c). However, **4a** is also formed and if its formation were competitive with the collapse mechanism, the product ratio should be dependent on solvent viscosity¹⁵ (k_d will decrease with respect to k_c as viscosity increases). However, we find that changing the solvent from benzene to *tert*-butylbenzene (a viscosity increase of *ca.* 45-fold) leads to no significant change in product ratio. This observation suggests that *trans*- $\text{Pt}(\text{CH}_2\text{C}_6\text{H}_5)\text{Br}(\text{PEt}_3)_2$ is *not* formed by path b. In this case, a competition between an $\text{S}_{\text{N}}2$ process (to form regular adduct) and a radical abstraction process (to produce dibromide) is indicated. For the reaction of benzyl chloride with **1a**, only the $\text{S}_{\text{N}}2$ path is operative because in comparing RCl vs. RBr reactivities, $\text{Cl/Br} \sim 10^{-2}$ for a nucleophilic displacement, whereas for a radical abstraction process $\text{Cl/Br} \sim 10^{-4}$. The radical process would then become noncompetitive for benzyl chloride.

A further example concerns α -haloester additions to **1a**. Using ethyl α -chloropropionate, the regular adduct is cleanly produced and occurs *via* a radical chain process.¹ In the corresponding α -bromoester reaction with **1a**, both regular adduct and dibromide are produced.¹⁶ However, *only* the regular adduct formation is inhibited by the presence of 5 mol % duroquinone. It appears here that the radical chain and abstraction processes are competitive, but the $\text{S}_{\text{N}}2$ process is not.

Summarizing, several possible routes exist for these reactions, and the choice of a particular path will depend on many factors, *e.g.*, the nature of the carbon-halogen linkage, the nucleophilicity of the metal complex, the ability of the metal complex to undergo one-electron processes (*i.e.*, relative positioning of oxidation levels and availability of suitable mechanisms for one-electron transfer), steric effects, and ligand exchange processes. A subtle balance of these factors will direct which path (if any) dominates the oxidative addition process.

Acknowledgments. This work has been supported by the Alfred P. Sloan Foundation (J.A.O.) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation in the form of a generous grant (GP 32317) for the XL-100 MHz nmr spectrometer.

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- (4) Separate experiments, in which the reactions of **2** or **3** with alkyl halide

under a variety of conditions were studied, showed **4** to be formed too slowly for such routes to be significantly involved here.

- (5) Although the radical trap *t*-BuNO has been used to study the reactions of $\text{Pt}(\text{PPh}_3)_3$ with CH_3I , $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$, and $\text{C}_2\text{H}_5\text{I}$,⁶ the results appear ambiguous in view of a recent report⁷ that *t*-BuNO actually induces radical decomposition of $\text{Pd}(\text{CH}_2\text{C}_6\text{H}_5)\text{Cl}(\text{PPh}_3)_2$. It should be noted, however, that **2a** is stable toward radical decomposition under the usual reaction conditions in the absence of *t*-BuNO.
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- (8) Reactions were carried out using 0.04–0.10 M solutions of **1**. ³¹P nmr spectroscopy (¹H noise decoupled, FT mode) enabled monitoring and product analysis of the reaction. Spectra were recorded at -55° in toluene (or benzene-toluene mixtures) to slow intermolecular phosphine exchange processes. Unambiguous identification of all complexes was possible by comparison of ³¹P nmr chemical shift and $J(^{195}\text{Pt}-^{31}\text{P})$ values with authentic samples. At -55° , in the presence of liberated PEt_3 , the hydrido and dihalide species are converted and detected as the corresponding cations, $[\text{PtH}(\text{PEt}_3)_3]^+\text{I}^-$ and $[\text{PtI}(\text{PEt}_3)_3]^+\text{I}^-$. When the reactions are carried out in toluene, small quantities of *trans*- $\text{Pt}(\text{CH}_2\text{C}_6\text{H}_5)(\text{PEt}_3)_2$ are also detected. Organic products were determined by glc and ¹H nmr spectroscopy.
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- (12) No CIDNP effects have been observed in the reaction of **1a** with the very reactive organic halides CH_3I , $\text{CH}_2=\text{CHCH}_2\text{Br}$, or $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$.
- (13) If the organic halide has a functional group which can bind to the metal, other paths are also possible. See J. A. Osborn in "Prospects in Organotransition-Metal Chemistry" (U.S.-Japan Monograph), Plenum Press, New York, N.Y., 1974; A. V. Kramer, unpublished results.
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- (16) Due to its extreme reactivity, even at -65° , we have not been able to detect CIDNP effects in this system. Interestingly, ³¹P nmr data at -55° indicate that in the radical chain path, the $[\text{CH}_3\text{CHCOOEt}]$ radical is competitively captured by **1a** at both carbon (to form the regular addition adduct) and oxygen. The O-bonded complex rearranges at ambient temperatures to the more stable regular (C-bonded) adduct.

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Received August 26, 1974

On the High-Spin-Low-Spin Equilibrium of Manganocene and Dimethylmanganocene

Sir:

Investigations concerning the nature of the electronic ground state of manganocene, $\text{Mn}(\text{cp})_2$, have been performed for more than 20 years.¹⁻¹² Among the metallocene series, $\text{Mn}(\text{cp})_2$ is of particular interest, because both high-spin, $a_{1g}^1e_{2g}^2e_{1g}^2({}^6A_{1g})$, and low-spin, $a_{1g}^2e_{2g}^3({}^2E_{2g})$ or $a_{1g}^1e_{2g}^4({}^2A_{1g})$, configurations could be realized in the ground state, depending on the magnitude of the axial ligand field splittings D_s and D_t .⁸⁻¹² In the fifties magnetic susceptibility (χ_m) measurements,¹⁻⁴ chemical evidence,¹⁻⁵ and esr results⁷ led to the conclusion that both $\text{Mn}(\text{cp})_2$ and related 1,1'-dimethylmanganocene, $\text{Mn}(\text{mecp})_2$, were "essentially ionic ($S = 5/2$) cyclopentadienides" in liquid and solid solutions as well as in pure solid state, in spite of some difficulties encountered in the interpretation of the anomalously small χ_m found in the pure solids at low temperatures. It was therefore somewhat surprising when in 1972 Rabalais, *et al.*,¹¹ reported a HeI photoelectron spectrum ascribed to gaseous $\text{Mn}(\text{cp})_2$ possessing a $e_{2g}^4a_{1g}^1({}^2A_{1g})$ ground state configuration. This interpretation was, however, criticized by Evans, *et al.*¹² The Oxford group¹² recently measured the HeI photoelectron spectra of both $\text{Mn}(\text{cp})_2$ and $\text{Mn}(\text{mecp})_2$, and using ligand field theoretical arguments came to the conclusion that gaseous $\text{Mn}(\text{cp})_2$ is essentially a high-spin (${}^6A_{1g}$) complex, while $\text{Mn}(\text{mecp})_2$