

disproportionate and that about 20% of them abstract hydrogen from HMPA. The higher ratio (42/21) observed from the reaction using pyrrolidine as both nucleophile and solvent merely reflects the relative ability of pyrrolidine and HMPA to donate hydrogen atoms to radicals. The production of essentially equimolar amounts of alkane and alkene in the reaction using acetate ion makes it clear that radical-nucleophile coupling leading to *tert*-butyl acetate occurs virtually to the exclusion of the hydrogen abstraction process. Further, the similar alkane/alkene ratio in the reaction using cyanide ion suggests that radical-nucleophile coupling is a major competing reaction in this case as well even though this is not reflected in the yield of coupling product. The possible further reaction of *t*-BuCN with its radical ion to give higher molecular weight products is being explored.

These results, examined with earlier findings,<sup>7</sup> indicate that the coupling of radicals with nucleophiles is a general reaction if *either* of the two reactants has a site of unsaturation which may be as simple as an isolated multiple bond. They also suggest, however, that the multiple bond must be adjacent to the atom being bonded. The mechanistic implication is that reaction will occur only if a reasonably low-lying antibonding orbital is available at the reaction site, a strong argument for the intermediacy of an adduct radical ion. The fate of the electron has not yet been determined although it is clear that its capture by R· is not an important process when HMPA is used as a solvent. It is very likely transferred to solvent, as noted in the reaction scheme, and leads ultimately to solvent decomposition products.<sup>11</sup>

It appeared reasonable that the variation in yields of RN might reflect the relative stabilities of RN radical ions, a postulate which in principle could be explored with polarographic measurements. Unfortunately, all three classes of compound require higher negative voltages for reduction than can be successfully applied with presently available solvents and supporting electrolytes.

We have no good estimate of the absolute efficiency of the coupling reaction. The fact that it competes favorably with disproportionation in the case of *tert*-butyl radical and with radical coupling and hydrogen abstraction in the case of *n*-butyl radical suggests that it is rather fast.

(11) G. Fraenkel, S. H. Ellis, and D. T. Dix, *J. Amer. Chem. Soc.*, **87**, 1406 (1965).

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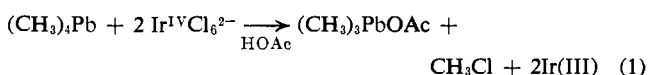
### Alkyl Transfers from Organometallic Compounds by One-Electron Processes

Sir:

The formation and cleavage of alkyl-metal bonds play an important role in the chemistry of organometallic intermediates involved in catalytic processes of organic as well as biochemical substrates. We wish to demonstrate the importance of electron transfer pro-

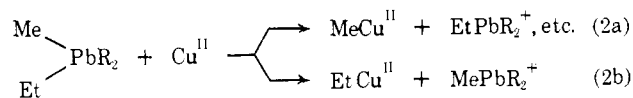
cesses as viable routes for reactions of alkyl-metals since charge transfer and other homolytic processes are little known<sup>1</sup> in contrast to the usual electrophilic mechanisms.<sup>2</sup>

As a model system, we examined alkyl transfers from a series of organoleads listed in Table I with hexachloroiridate(IV), which is known to participate in outer-sphere oxidations involving one-electron changes.<sup>3</sup> For example, the oxidative cleavage of tetraethyllead by Ir<sup>IV</sup>Cl<sub>6</sub><sup>2-</sup> occurs rapidly at 25° with a 1:2 stoichiometry in acetic acid or acetonitrile solutions to afford ethyl chloride and chloroiridium(III). Similarly, only one alkyl group is readily cleaved from the other tetraalkylleads [PbMe<sub>n</sub>Et<sub>4-n</sub>]. The lead species from tetramethyllead in acetic acid can be identified as trimethyllead acetate by quantitative pmr analysis of the reaction mixture.



The rates were followed in acetonitrile by the disappearance of IrCl<sub>6</sub><sup>2-</sup> spectrophotometrically and showed a first-order kinetic dependence on each reactant.

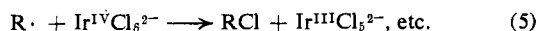
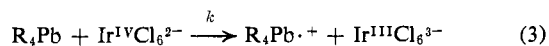
Two important criteria can be used to distinguish the reaction with Ir<sup>IV</sup>Cl<sub>6</sub><sup>2-</sup> from the more conventional electrophilic processes, *e.g.*, with Ag<sup>I</sup>, Cu<sup>I</sup>,<sup>11</sup> complexes, etc.<sup>4</sup> First, the rate of reaction of PbMe<sub>n</sub>Et<sub>4-n</sub> with IrCl<sub>6</sub><sup>2-</sup> increases successively as methyl is replaced by ethyl groups (see *n* = 4-0 in Table I, column 2). Second, a given ethyl group is cleaved approximately 25 times faster than a methyl group (column 5). Both of these reactivity trends are diametrically opposed to an electrophilic cleavage such as reaction 2 with chloro-



copper(II). Thus, preferential attack by the copper(II) electrophile occurs directly at the less hindered methyl site by a factor of 44.<sup>4b,d,e</sup>

These results suggest that the rate-limiting step with IrCl<sub>6</sub><sup>2-</sup> occurs prior to alkyl transfer, and we propose the mechanism given in Scheme I in which the slow step

#### Scheme I



(1) Cf. (a) P. Abley, E. R. Dockal, and J. Halpern, *J. Amer. Chem. Soc.*, **94**, 659 (1972); (b) J. H. Espenson and J. S. Shveima, *ibid.*, **95**, 4468 (1973); (c) A. van den Bergen and B. O. West, *Chem. Commun.*, **52**, (1971); (d) D. Dodd and M. D. Johnson, *J. Organometal. Chem.*, **52**, 1 (1973).

(2) M. H. Abraham in "Comprehensive Chemical Kinetics," Vol. 12, C. H. Bamford and C. F. Tipper, Ed., Elsevier, Amsterdam, 1972.

(3) J. Halpern, R. J. Legare, and R. Lumry, *J. Amer. Chem. Soc.*, **85**, 680 (1963); J. Halpern and M. Pribanić, *ibid.*, **90**, 5942 (1968); P. Abley and J. Halpern, *Chem. Commun.*, 1238 (1971).

(4) (a) N. Clinton and J. K. Kochi, *J. Organometal. Chem.*, **42**, 229 (1972); (b) *ibid.*, **56**, 243 (1973); (c) *ibid.*, **61**, 433 (1973); (d) *ibid.*, **56**, 227 (1973); (e) The stoichiometry of the reaction of tetraalkyllead with copper(II) chloride is the same as that for iridium(IV) in eq 1. Alkyl chlorides are formed subsequent to homolysis of the alkylcopper(II) intermediates in eq 2 by ligand transfer with copper(II) chloride, *e.g.*

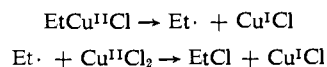


Table I. Reactivity Parameters for  $\text{PbMe}_n\text{Et}_{4-n}$  and  $\text{IrCl}_6^{2-}$ 

$\text{PbMe}_n\text{Et}_{4-n}$	$k,^a$ l./mol sec	Alkyl chloride (mmol) <sup>b</sup>		EtCl/ MeCl <sup>c</sup>	IP, <sup>d</sup> eV	$E,^e$ V
		EtCl	MeCl			
$\text{PbEt}_4$	25	0.101			8.13	1.67
$\text{PbEt}_3\text{Me}$	11	0.104	0.0015	24	8.26	1.75
$\text{PbEt}_2\text{Me}_2$	3.3	0.101	0.0040	25	8.45	1.83
$\text{PbEtMe}_3$	0.57	0.092	0.012	24	8.65	2.00
$\text{PbMe}_4$	0.02		0.105		8.90	2.13

<sup>a</sup> In  $\text{CH}_3\text{CN}$  at  $36^\circ$ . Second-order rate constant detected spectrophotometrically at 490 and 585 nm ( $\epsilon$  5250 and  $410 \text{ M}^{-1} \text{ cm}^{-1}$ , respectively) in concentration range  $[\text{IrCl}_6^{2-}] = 5 \times 10^{-5}$  to  $2 \times 10^{-3} \text{ M}$ ,  $[\text{PbR}_4] = 2 \times 10^{-5}$  to  $2 \times 10^{-2} \text{ M}$  with  $1.0 \text{ F LiClO}_4$ . <sup>b</sup>  $\text{Na}_2\text{IrCl}_6$  (0.200 mmol) and  $\text{PbR}_4$  (0.100 mmol) in 3 ml of  $\text{CH}_3\text{CN}$ , measured by glc. <sup>c</sup> Statistically corrected. <sup>d</sup> By  $\text{He}^I$  pes. <sup>e</sup> Potential vs.  $\text{Ag}/\text{AgCl}$  reference at  $i/a = 1.0 \text{ mA/cm}^{-2}$  with  $2.0 \times 10^{-3} \text{ M PbR}_4$  and  $0.23 \text{ F LiBF}_4$  in  $\text{CH}_3\text{CN}$  at  $22^\circ$ .

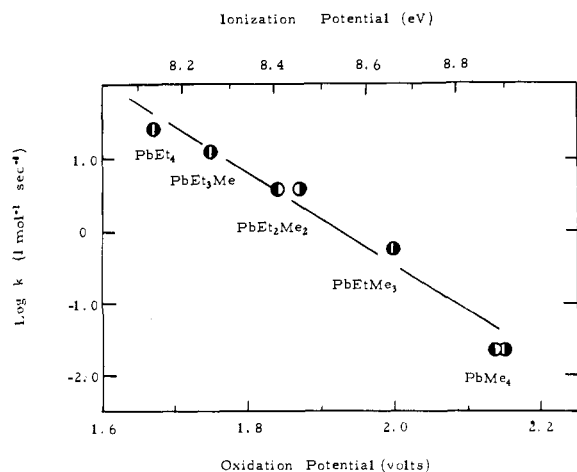


Figure 1. Correlation of the rates of oxidation of  $\text{PbMe}_n\text{Et}_{4-n}$  by  $\text{IrCl}_6^{2-}$  in acetonitrile with the (arbitrary) electrochemical oxidation potential  $\bullet$  (lower scale) and the vertical ionization potential  $\circ$  (upper scale).

3 involves charge transfer. Indeed, there is a reasonable linear correlation of the rates ( $\log k$ ) with the one-electron oxidation potentials determined by chronopotentiometry<sup>5</sup> as shown in Figure 1. The oxidation potentials of  $\text{PbMe}_n\text{Et}_{4-n}$  are related to the electron-detachment process



and there is also a striking relationship with the vertical ionization potentials determined by  $\text{He}(I)$  photoelectron spectroscopy.<sup>6</sup>

Selectivity in the transfer of alkyl groups according to Scheme I occurs during fragmentation of the cation radical in a fast subsequent step, which is consistent with the results of a mass spectral study.<sup>4b</sup> Thus, a quantitative determination of the cracking patterns of the series of  $\text{PbMe}_n\text{Et}_{4-n}$  showed that scission of the Et-

(5) The values of  $n$  were determined in  $5 \times 10^{-3} \text{ M PbR}_4$  in acetonitrile using thin-layer chronopotentiometry at a Pt anode. See D. G. Peters in "Standard Methods of Instrumental Analysis," Part A, F. J. Welcher, Ed., Van Nostrand, Princeton, New Jersey, 1968, Chapter 21. (b) The oxidation potentials were determined in magnetically stirred solutions containing  $2 \times 10^{-3} \text{ M PbR}_4$  and  $0.23 \text{ F LiBF}_4$  in acetonitrile. Current reversal chronopotentiometry showed that the one-electron oxidation wave was irreversible. The potentials measured at constant current density reflect the relative ease of removal of the first electron from  $\text{PbR}_4$ .

(6) (a) H. C. Gardner, C. H. McFarland, G. Mateescu, D. G. Peters, and J. K. Kochi, unpublished results; (b) For pes of group IVb tetramethyls, see A. E. Jonas, *et al.*, *J. Electron Spectrosc. Relat. Phenomena*, **1**, 29 (1972); S. Evans, *et al.*, *J. Chem. Soc., Faraday Trans. 2*, **68**, 905 (1972); (c)  $\text{PbR}_4$  also forms charge transfer complexes with TCNE similar to those recently observed with polysilanes (V. F. Traven and R. West, *J. Amer. Chem. Soc.*, **95**, 6824 (1973); H. Sakurai, *et al.*, *ibid.*, **95**, 6826 (1973)).

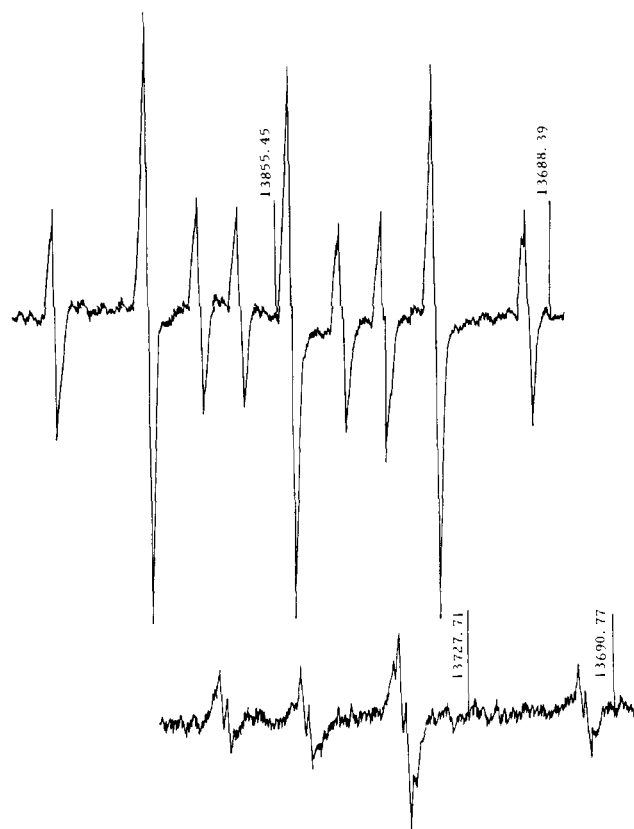
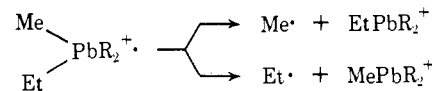


Figure 2. The esr spectrum of the spin adduct of ethyl radical to NB from the reaction of  $\text{PbEt}_4$  and  $\text{IrCl}_6^{2-}$  in acetic acid at room temperature. The inset below is the low-field portion of the spectrum at higher resolution showing resolved  $\gamma$ -proton splittings from the ethyl group [ $a_N = 16.52$ ,  $a_{\beta\text{H}} = 10.67$ ,  $a_{\gamma\text{H}} = 0.37 \text{ G}$ ]. Nmr field markers are in kHz.

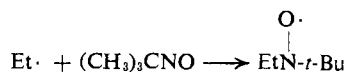
Pb bond is favored over the Me-Pb bond in the parent



molecular ions, largely due to bond energy differences.<sup>4b</sup>

Examination of the electron spin resonance spectrum during the reaction with  $\text{IrCl}_6^{2-}$  did not reveal the presence of the cation radical  $\text{PbEt}_4^{\cdot+}$ , which must be highly unstable even at temperatures as low as  $-20^\circ$ . Nonetheless, the formation of ethyl radicals in high yields was evident from spin-trapping experiments<sup>7</sup> with nitrosoisobutane (NB) and phenyl-*t*-butylnitron. The well-resolved spectrum in Figure 2 of the ethyl adduct to NB is a relevant example.

(7) E. G. Janzen, *Accounts Chem. Res.*, **4**, 31 (1971).



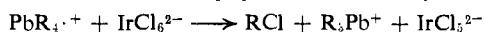
The use of  $\text{IrCl}_6^{2-}$  as an efficient scavenger for alkyl radicals is implied in Scheme I (eq 5) by the isolation of alkyl chlorides in high yields (even in the presence of a hundredfold excess of bromide ion<sup>8</sup>). In support, separate experiments do show that ethyl radicals generated unambiguously from the thermolysis of propionyl peroxide are quantitatively converted by  $\text{IrCl}_6^{2-}$  to ethyl chloride.<sup>9</sup>

The reaction mixture consisting of reduced iridium(III) species was reoxidized with either chlorine or lead dioxide, and the iridium(IV) was separated by silica gel chromatography. We deduce from the subsequent analysis of  $\text{Ir}^{\text{IV}}\text{Cl}_6^{2-}$  that one-half of the iridium(III) formed in the reaction consisted of  $\text{Ir}^{\text{III}}\text{Cl}_6^{3-}$  in accord with eq 3 of Scheme I. The remainder of the iridium(III) appears as an insoluble polynuclear species and the fate of  $\text{Ir}^{\text{III}}\text{Cl}_5^{2-}$  formed in eq 5 has not yet been clarified.

**Acknowledgment.** We wish to thank Dr. D. G. Peters for helpful advice, Dr. I. Elson for the spin trapping experiments, and the National Science Foundation for financial support.

(8) Added as the quaternary ammonium salt. Compare S. N. Anderson, D. H. Ballard, J. Z. Chrzastowski, D. Dodd, and M. D. Johnson, *J. Chem. Soc., Chem. Commun.*, 685 (1972).

(9) The spin trapping experiments in Figure 2 suggest that alkyl radicals are intermediates, and we consider the alternative formulation below for the concertedness of eq 4 plus 5 to be less likely. The distinc-



tion rests on the metastability of the cation radical in eq 4, which is supported by our inability to observe the esr spectra of  $\text{PbR}_4\cdot^+$  and the irreversibility of the electron transfer step in the electrochemical oxidation<sup>5</sup>.

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## Synthesis of Bis(triethylphosphine) Organonickel and Organopalladium Complexes Employing Nickel and Palladium Atoms as Synthetic Reagents<sup>1</sup>

Sir:

Herein we describe some procedures for the use of nickel atoms and palladium atoms as reagents for the synthesis of a variety of organometallic complexes, where these atoms are capable of oxidative insertion<sup>2</sup> into carbon-halogen, carbon-carbon, and carbon-oxygen bonds. General metal atom techniques have been described both by Timms<sup>3a</sup> and Skell, *et al.*,<sup>3b</sup> and a detailed description of our apparatus will be forthcoming.<sup>4</sup>

For aryl halides, we have condensed nickel atoms with excess chloropentafluorobenzene and triethylphosphine at  $-196^\circ$ . Pump-off of volatiles left a dark solid which was washed with  $\text{CH}_2\text{Cl}_2$ , filtered,

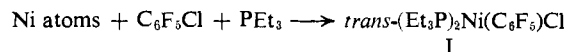
(1) Metal Atom Reactions with Fluorocarbons. V. For Part IV in the series, see K. J. Klabunde and H. F. Efner, *J. Fluorine Chem.*, **4**, 115 (1964).

(2) Alternative terminology: "oxidative addition" of carbon-halogen, carbon-carbon, and carbon-oxygen bonds to metal atoms.

(3) (a) P. L. Timms, *Advan. Inorg. Chem. Radiochem.*, **14**, 121 (1972); (b) P. S. Skell, D. L. Williams-Smith, and M. J. McGlinchey, *J. Amer. Chem. Soc.*, **95**, 3337 (1973); P. S. Skell, J. J. Havel, and M. J. McGlinchey, *Accounts Chem. Res.*, **6**, 97 (1973).

(4) K. J. Klabunde and H. F. Efner, *Inorg. Chem.*, submitted for publication.

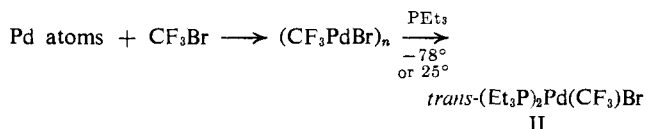
decolorized with carbon, and  $\text{CH}_2\text{Cl}_2$  pumped off, and the resultant solid was crystallized from hexane- $\text{CH}_2\text{Cl}_2$  yielding 0.29 g (55% based on metal vaporized<sup>5</sup>) of yellow *trans*-bis(triethylphosphine)pentafluorophenylnickel chloride (I): mp  $111-112^\circ$  (lit.  $112-113^\circ$ );<sup>6</sup>



mass spectral (24 eV) (Parent (6%); Parent -  $\text{C}_6\text{F}_5$ , Cl (5);  $\text{C}_6\text{F}_5\text{PEt}_3$  (100);  $\text{C}_6\text{F}_5$  (3);  $\text{ClPEt}_3$  (25);  $\text{PEt}_3$  (9)).

Lower yields of I could be obtained by cocondensing nickel atoms and chloropentafluorobenzene and warming to  $-78^\circ$ , followed by triethylphosphine addition, which shows that the nonligand stabilized species  $(\text{C}_6\text{F}_5\text{NiCl})_n$  is stable at  $-78^\circ$ .

For alkyl halides, palladium atoms were cocondensed with trifluoromethyl bromide at  $-196^\circ$ , followed by slow warming to  $-78^\circ$  with pump-off of excess substrate. Then triethylphosphine and  $\text{CH}_2\text{Cl}_2$  were condensed into the reactor followed again by warming, stirring, pumping off, washing the solid residue with acetone, filtering, decolorizing, pumping off, and crystallizing the resultant solid from methanol yielding 0.04 g (7%<sup>5</sup>) of white *trans*-bis(triethylphosphine)trifluoromethylpalladium bromide (II): mp  $96-97$ ;



Calcd: C, 31.75; H, 6.16; F, 11.59; Found: C, 31.64; H, 6.27; F, 11.54. Mass spectral (24 eV) [Parent (5%); Parent -  $\text{CF}_3$  (4); Parent -  $\text{CF}_3$ , Cl (24);  $\text{BrPEt}_3$  (100);  $\text{PEt}_3$  (43)]; nmr ( $\text{CDCl}_3$ ) quintet ( $\delta$  1.18,  $J_{\text{H,P-CH}_3} = 8.0$  Hz, 6 H) multiplet ( $\delta$  2.0, 4 H);<sup>7</sup> ir  $\text{cm}^{-1}$  (acetone) 3020 m, 1467 m, 1263 m, 1090 vs, 1046 vs, 1002 vs, 778 s, 738 s, 551 s, 406 w. It is remarkable that essentially the same yield of II was obtained when, after the atom reaction, the reactor was warmed and vented to air and the acetone soluble residue washed, filtered, and followed by triethylphosphine addition. This experiment showed that the  $(\text{CF}_3\text{PdBr})_n$  intermediate is stable to air at room temperature in acetone solution or the solid state.

Simultaneous condensation of palladium atoms, trifluoromethyl bromide, and triethylphosphine did not improve the yield of II, although this technique markedly improves the yield in aryl halide systems and perfluoroolefin systems (*vide infra*).

For acyl halides, palladium atoms were cocondensed with heptafluorobutyryl chloride followed by slow warming to  $-78^\circ$  with pump-off of excess substrate and then adding of triethylphosphine-acetone, stirring, and pumping off. The resultant solid residue was washed with acetone and the solution filtered, decolorized, and pumped to dryness, to yield 0.11 g (15%<sup>5</sup>) of yellow oil *trans*-bis(triethylphosphine)heptafluorobutyrylpalladium chloride (III): mass spectral (24 eV) [Parent (16%); Parent -  $\text{C}_3\text{F}_7$ , Cl (100); Parent -  $\text{C}_3\text{F}_7\text{CO}$  (100); Parent -  $\text{C}_3\text{F}_7\text{CO}$ , Cl (60);  $\text{C}_3\text{F}_7$  (7);

(5) Assuming about 60% of the metal vaporized reaches the reaction zone.

(6) J. R. Phillips, D. T. Rosevear, and F. G. A. Stone, *J. Organometal. Chem.*, **2**, 455 (1964).

(7) Geometry shown by nmr: J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc., London*, 279 (1963); F. J. Hopton, A. J. Rest, D. T. Rosevear, and F. G. A. Stone, *J. Chem. Soc. A*, 1326 (1966).