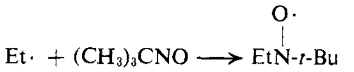

$$\mathrm{Et}\cdot + (\mathrm{CH_3})_3\mathrm{CNO} \longrightarrow \mathrm{Et}\overset{\mathrm{O}\cdot}{\overset{|}{\mathrm{N}}}\text{-}t\text{-}\mathrm{Bu}$$

The use of $IrCl_6^{2-}$ 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[8]). In support, separate experiments do show that ethyl radicals generated unambiguously from the thermolysis of propionyl peroxide are quantitatively converted by $IrCl_6^{2-}$ to ethyl chloride.[9]

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 $Ir^{IV}Cl_6^{2-}$ that one-half of the iridium(III) formed in the reaction consisted of $Ir^{III}Cl_6^{3-}$ in accord with eq 3 of Scheme I. The remainder of the iridium(III) appears as an insoluble polynuclear species and the fate of $Ir^{III}Cl_5^{2-}$ 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.

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[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 distinction

$$\mathrm{PbR_4\cdot^+} + \mathrm{IrCl_6^{2-}} \longrightarrow \mathrm{RCl} + \mathrm{R_3Pb^+} + \mathrm{IrCl_5^{2-}}$$

tion rests on the metastability of the cation radical in eq 4, which is supported by our inability to observe the esr spectra of $PbR_4\cdot^+$ and the irreversibility of the electron transfer step in the electrochemical oxidation[5].

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Synthesis of Bis(triethylphosphine) Organonickel and Organopalladium Complexes Employing Nickel and Palladium Atoms as Synthetic Reagents[1]

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[2] into carbon–halogen, carbon–carbon, and carbon–oxygen bonds. General metal atom techniques have been described both by Timms[3a] and Skell, *et al.*,[3b] and a detailed description of our apparatus will be forthcoming.[4]

For aryl halides, we have condensed nickel atoms with excess chloropentafluorobenzene and triethylphosphine at −196°. Pump-off of volatiles left a dark solid which was washed with CH_2Cl_2, filtered, decolorized with carbon, and CH_2Cl_2 pumped off, and the resultant solid was crystallized from hexane–CH_2Cl_2 yielding 0.29 g (55% based on metal vaporized[5]) of yellow *trans*-bis(triethylphosphine)pentafluorophenylnickel chloride (I): mp 111–112° (lit. 112–113°);[6]

$$\text{Ni atoms} + \mathrm{C_6F_5Cl} + \mathrm{PEt_3} \longrightarrow \underset{\mathrm{I}}{trans\text{-}(\mathrm{Et_3P})_2\mathrm{Ni}(\mathrm{C_6F_5})\mathrm{Cl}}$$

mass spectral (24 eV) (Parent (6%); Parent − C_6F_5, Cl (5); $C_6F_5PEt_3$ (100); C_6F_5 (3); $ClPEt_3$ (25); PEt_3 (9)).

Lower yields of I could be obtained by cocondensing nickel atoms and chloropentafluorobenzene and warming to −78°, followed by triethylphosphine addition, which shows that the nonligand stabilized species $(C_6F_5NiCl)_n$ is stable at −78°.

For alkyl halides, palladium atoms were cocondensed with trifluoromethyl bromide at −196°, followed by slow warming to −78° with pump-off of excess substrate. Then triethylphosphine and CH_2Cl_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%[5]) of white *trans*-bis(triethylphosphine)trifluoromethylpalladium bromide (II): mp 96–97;

$$\text{Pd atoms} + \mathrm{CF_3Br} \longrightarrow (\mathrm{CF_3PdBr})_n \xrightarrow[-78^\circ \text{ or } 25^\circ]{\mathrm{PEt_3}} \underset{\mathrm{II}}{trans\text{-}(\mathrm{Et_3P})_2\mathrm{Pd}(\mathrm{CF_3})\mathrm{Br}}$$

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 − CF_3 (4); Parent − CF_3, Cl (24); $BrPEt_3$ (100); PEt_3 (43)]; nmr ($CDCl_3$) quintet (δ 1.18, $J_{\mathrm{H,P-CH_3}} = 8.0$ Hz, 6 H) multiplet (δ 2.0, 4 H);[7] ir 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 $(CF_3PdBr)_n$ 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° 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%[5]) of yellow oil *trans*-bis(triethylphosphine)heptafluorobutyrylpalladium chloride (III): mass spectral (24 eV)[Parent (16%); Parent − C_3F_7, Cl (100); Parent − C_3F_7CO (100); Parent − C_3F_7CO, Cl (60); C_3F_7 (7);

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[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.

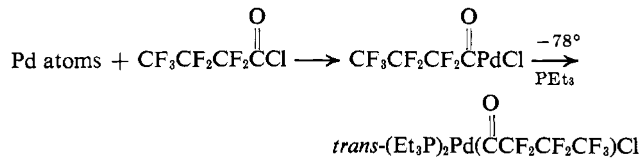
[3] (a) P. L. Timms, *Advan. Inorg. Chem. Radiochem.*, **14**, 121 (1972); (b) P. S. Skell, D. L. Williams-Smith, and M. J. McGlinchey, *J. Amer. Chem. Soc.*, **95**, 3337 (1973); P. S. Skell, J. J. Havel, and M. J. McGlinchey, *Accounts Chem. Res.*, **6**, 97 (1973).

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

[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).

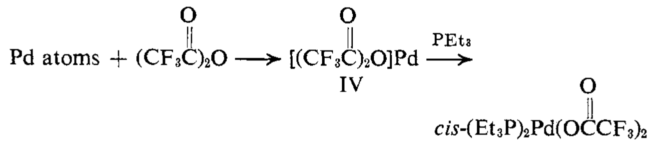


$$\text{Pd atoms} + CF_3CF_2CF_2\overset{\overset{O}{\|}}{C}Cl \longrightarrow CF_3CF_2CF_2\overset{\overset{O}{\|}}{C}PdCl \xrightarrow[PEt_3]{-78°} \textit{trans-}(Et_3P)_2Pd(\overset{\overset{O}{\|}}{C}CF_2CF_2CF_3)Cl$$

III

PEt₃ (100); HPEt₂ (60)]; ir (cm⁻¹) (acetone) 2985 vs, 1695 s, 1470 s, 1430 m, 1342 s, 1235 vs, 1195 vs, 1065 s, 1042 vs, 1030 vs, 1017 s, 772 vs, 732 s, 554 s, 319 s, 292 s; nmr ($CDCl_3$) quintet (δ 1.17, $J_{H,P-CH_3} = 7.6$ Hz, 6 H), multiplet (δ 1.83, 4 H).[7]

For acid anhydrides, palladium atoms were cocondensed with hexafluoroacetic anhydride at −196°. During deposition a small amount of noncondensable gas was evolved. The resultant matrix was slowly warmed to 25°. During warm-up the initially black matrix progressively changed to deep blue and then to brown as the excess substrate was pumped off. The resultant brown solid did not change in appearance on exposure to air and was washed out with diethyl ether. This solution continually precipitated palladium metal over a 1-hr period leaving a light yellow solution after filtration. Addition of triethylphosphine to this solution yielded a small amount of bis(triethylphosphine)-perfluorodiacetatopalladium (V).



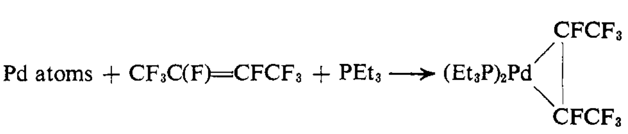
$$\text{Pd atoms} + (CF_3\overset{\overset{O}{\|}}{C})_2O \longrightarrow \underset{\text{IV}}{[(CF_3\overset{\overset{O}{\|}}{C})_2O]Pd} \xrightarrow{PEt_3} \textit{cis-}(Et_3P)_2Pd(O\overset{\overset{O}{\|}}{C}CF_3)_2$$

V

In another experiment the intermediate palladium compound IV was trapped by triethylphosphine before removal from the reactor. This yielded V using the usual isolation procedures as white crystals from a benzene–hexane mixture: 0.15 g (15%[5]); mp 151–152°; mass spectral (24 eV) [Parent (1%); Parent − CF_3CO_2 (5); $FPd(PEt_3)_2$ (10); $Pd(PEt_3)_2$ (43); $Pd(PEt_3)PEt_2$(16); $Pd(PEt_3)CO_2F$ (9); $CF_3CO_2PEt_3$ (100); $PdPEt_2$ (63)]; nmr ($CDCl_3$) doublet of triplets (δ 1.23, 6 H, $J_{CH_2-CH_3} = 7$ Hz, $J_{P-CH_3} = 18$ Hz), quintet (δ 1.88, 4 H, $J_{P-CH_2} = 8$ Hz);[7] ir cm⁻¹ (acetone) 2980 w, 1680 vs, 1390 m, 1280 vs, 1136 s, 830 m, 738 s, 710 s, 553 s, 400 w.

Intermediate IV must not be perfluorodiacetatopalladium [$(CF_3CO_2)_2Pd$] since this compound is known and is quite stable,[8] whereas IV is not stable. We do not yet know the structure of IV, although in view of its facile decomposition to yield palladium metal, and the cis geometry of the trapping product V, a Pd(O) complex with $(CF_3CO)_2O$ is likely.

In perfluoroolefin reactions, palladium atoms add to the carbon–carbon π-bonds. Thus, palladium atoms were condensed simultaneously with octafluoro-2-butene and triethylphosphine. On slow warming to 25°, the excess butene and phosphine were pumped off. The remaining yellow solid was washed with CH_2Cl_2, the solution filtered, decolorized, and pumped to dryness, and the resultant solid crystallized from pentane yielding pale yellow octafluoro-2-butenebis(triethylphosphine)palladium (VI): 0.55 g (56%[5]); mp 66–67°; Calcd: C, 35.40; H, 5.54; F, 28.03; Found: C, 35.17; H, 5.56; F, 27.81; mass spectral (24 eV)



VI

[$Pt(PEt_3)_2$ (100%); $Pd(PEt_3)$ $PHEt_2$ (27); $Pd(PEt_3)H_2$-PEt (21); $PdPEt_3$ (15); C_4F_8 (21); C_4F_7 (12); C_3F_5 (30); PEt_3 (57); CF_3 (15)]; nmr ($CDCl_3$) doublet of triplets (δ 1.05, 6 H, $J_{CH_2-CH_3} = 6.8$, $J_{P-CH_3} = 15.8$ Hz), quintet (δ 1.75, 4 H, $J_{P-CH_2} \sim 7$ Hz); ir cm⁻¹ (neat) 2978 vs, 2943 s, 2920 s, 2887 s, 1462 s, 1420 m, 1397 m, 1380 s, 1331 m, 1290 vs, 1270 vs, 1255 vs, 1180 vs, 1135 vs, 1039 vs, 100 s, 912 m, 886 m, 762 s, 738 m, 720 s, 704 m.

The palladium–perolefin intermediate is stable at −90° as shown by an experiment where palladium atoms and octafluoro-2-butene were cocondensed at −196° followed by warming to −90° and pump-off of excess butene. Then triethylphosphine was added and VI was isolated in 30% yield. If the intermediate was allowed to warm to approximately −20°, decomposition occurred to give back olefin and palladium metal (average ratio of olefin : metal = 3 : 1).

A detailed discussion of the mechanisms of these reactions must be delayed until further data are obtained. However, it is interesting to note that after examining a host of R–X + Ni, Pd atom oxidative insertions we know that (1) RMX is definitely formed at low temperature (before phosphine addition and trapping) and (2) phosphine trapping always yields trans complexes (such as compounds I, II, and III). The trans geometry is sterically favored over cis, so the phosphine addition to RMX probably occurs in a stepwise and selective manner. In the cases where RX, Et_3P, and M atoms are all condensed together, RMX formation may not occur first. It would be quite reasonable to expect, for example, that $Ni(PEt_3)_4$ could be formed and then react with RX to yield the observed products. However, this sequence is not likely since hydrogen is evolved in a Ni + PEt_3 reaction,[9] which we do not observe in Ni, PEt_3, and RX simultaneous depositions.

Overall, these examples illustrate the wide scope in organometallic synthesis using nickel and palladium atoms, and, once a laboratory metal atom reactor is obtained, compare favorably with normal methods for making these types of complexes.[10] Forthcoming reports from our laboratory will describe these areas in more detail with emphasis on production and study of reactive organometal intermediates involved in numerous synthetic schemes.

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