Novel Synthesis of σ-Bonded Palladium and Nickel Compounds by Co-condensation of Metal Vapour with Alkyl Free Radicals

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Summary The novel compounds *trans*-$(CF_3)_2Pd(PMe_3)_2$ and $(CF_3)_2Ni(PMe_3)_3$ have been prepared by co-condensation of palladium and nickel with trifluoromethyl radicals; initially the thermally unstable unsaturated alkyls $Pd(CF_3)_2$ and $Ni(CF_3)_2$ were prepared which were subsequently stabilized by trapping with trimethylphosphine at low temperature.

We have recently described the synthesis of a variety of main-group organometallic compounds formed from the reaction of metal vapour and free radicals. These radicals were produced by using a radio-frequency glow discharge homolytically to cleave symmetric molecules at their central, weakest bond. Trifluoromethyl, methyl, and trifluorosilyl radicals were generated in this manner, and co-condensation of these species on to a surface at −196 °C with elements such as Hg, Se, Sn, Te, Cd, and Bi yielded a number of σ-bonded compounds.[1]

Here we report the first preparation of transition metal complexes by this technique, to give *trans*-$(CF_3)_2Pd(PMe_3)_2$ and $(CF_3)_2Ni(PMe_3)_3$. These compounds are produced by combining metal vapour and plasma-generated free radicals to form co-ordinatively unsaturated intermediates of the type $M(CF_3)_2$, followed by phosphine trapping at low temperature (Scheme). The reactive, unsolvated species $M(CF_3)_2$ are examples of 'electron deficient' metal perfluoroalkyls of marginal stability even at low temperatures. In some cases one can observe the decomposition of such unsaturated organometallic species by following their ^{19}F or ^{1}H n.m.r. spectra as temperature is increased.[2]

$$\text{Pd atoms} + 2CF_3\cdot \xrightarrow{\text{i}} Pd(CF_3)_2 \xrightarrow{\text{ii}} \textit{trans}\text{-}(CF_3)_2Pd(PMe_3)_2$$

$$\text{Ni atoms} + 2CF_3\cdot \xrightarrow{\text{i}} Ni(CF_3)_2 \xrightarrow{\text{iii}} (CF_3)_2Ni(PMe_3)_3$$

Scheme. Reagents and conditions: i, −196 °C; ii, −78 °C, $+PMe_3$; iii, −100 °C, $+PMe_3$.

Palladium metal (0·138 g) was co-condensed with CF_3 radicals on to a surface at −196 °C; the matrix was warmed to −78 °C and volatile products were pumped off. Trimethylphosphine and dichloromethane were then sequentially condensed into the reaction, followed by warming to room temperature. Pentane extraction of the solid residues gave 78 mg of crude products (16% yield based on metal vaporized). Repeated crystallization from pentane produced white, air-stable needles, decomp. 180 °C. The ^{19}F n.m.r. spectrum showed a triplet† (J 21 ± 1 Hz) at 18·3 p.p.m (external reference $CFCl_3$) while the $\{^{1}H\}^{31}P$ n.m.r. spectrum contained a septet (J 22 ± 1 Hz) at −12·0 p.p.m. (external reference 85% H_3PO_4). The ^{1}H n.m.r. spectrum consisted of a triplet at δ 1·07 characteristic of *trans*-phosphine groups. Mass spectral analysis gave an envelope of peaks for $(PMe_3)_2Pd(CF_3)^+$ corresponding to the abundance of the five major isotopes of palladium, and elemental analyses

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† All n.m.r. experiments done in $[^{2}H_6]$benzene, except where noted.

were satisfactory. The compound may be sublimed at 50 °C (10^{-4} Torr).

The nickel compound was similarly synthesized. After warming to room temperature and overnight pumping, the solid residue was extracted with pentane, and the solution filtered through Norit. Crystallization from pentane produced 90 mg (21% yield) of orange needles, m.p. 117—119 °C. At 30 °C, the ^{19}F n.m.r. spectrum‡ showed a broad singlet, while at −35 °C the signal resolved into a quartet at 7·4 p.p.m. (J 28 Hz ± 1). This temperature-dependent behaviour is similar to that of the known compound $Me_2Ni(PMe_3)_3$, and indicates the 'freezing out' of a trigonal bipyramidal conformation with axial CF_3 groups.[3] An ambient temperature $\{^1H\}^{31}P$ n.m.r. study showed a broad singlet at −20·1 p.p.m. and the ^{1}H n.m.r. spectrum consisted of a singlet at δ 1·36. Mass spectral analysis showed sets of peaks for $(PMe_3)_3Ni(CF_3)^+$ and $(PMe_3)_2Ni(CF_3)(CF_2)^+$, each corresponding to the abundances of the two nickel isotopes, and elemental analyses were satisfactory. The compound sublimed at 25 °C (10^{-4} Torr).

The stability of unsolvated R_2M and RMX species is dependent upon both the metal and the nature of the organic groups; the contrast between metals is demonstrated in $Pd(CF_3)_2$ and $Ni(CF_3)_2$. Phosphine trapping experiments show that $Pd(CF_3)_2$ has a finite lifetime at room temperature. The nickel analogue was trapped at −100 °C, after we found that trapping at −78 °C gave a mixture of perfluoromethyl and perfluoroethyl complexes. The formation of perfluoroethyl compounds is currently under investigation; we speculate that the unstable $Ni(CF_3)_2$ eliminates difluorocarbene, which intramolecularly inserts into the $M–CF_3$ bond.

$Ni(CF_3)_2$ may be compared with the catalytically useful $Ni(acac)_2–AlMe_3$ system (Hacac = pentanedione), where a highly unstable (decomp. below −130 °C) $NiMe_2$ species is thought to form.[4] Isolable, NiR_2 complexes are also known,[5] which are even stable in the air. Klabunde and Low have previously reported the co-condensation of Pd atoms with a series of alkyl and aryl halides which oxidatively add to form species of the type RPdX, generally isolated as the phosphine adducts $(Et_3P)_2Pd(R)X$. While CF_3PdI had a finite lifetime at room temperature in air, the existence of CH_3PdI was only inferred from decomposition gases evolved upon matrix warm-up [low temperature phosphine trapping experiments failed to yield $(Et_3P)_2PdMeI$].[6]

Recent work has shown evidence for the formation of other less stable transition metal complexes using SiF_3, PMe_2, CF_3, and CH_3 radicals;[7] we expect that the $M(CF_3)_2$ species will be precursors for a variety of arene and olefin complexes of the general formulae $R_2M(\eta^6\text{-arene})$ and R_2ML_2.

The compound $(CF_3)_2Pd(PR'_3)_2$ has also been recently prepared by Morrison and Krause by a trifluoromethyl transfer reaction using the unusual reagent $Cd(CF_3)(glyme)_2$.[8] The metal vapour-free radical technique is thought to be a more general synthetic method, because for many σ-bonded ligands no such transfer reagent is known, and many transfer reactions will not proceed rapidly until well past the point of thermal stability for the desired ligand-stabilized alkyl product.

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‡ CF_2Cl_2 solvent.

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