# Comparative Stabilities and Metal–Carbon Bond Distances for Some $\sigma$-Arylnickel Complexes

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AFTER the initial reports[1,2] of pentafluorophenyl derivatives of transition metals, a considerable number of these species has been described.[3] Compared to transition-metal phenyls, the analogous pentafluorophenyl and pentachlorophenyl[4–6] complexes exhibit considerably increased thermal and oxidative stabilities. Since the greater stability of transition-metal perfluoroalkyls (*vis à vis* the corresponding alkyls) is associated with a shorter metal–carbon bond length,[7,8] it was decided to study in detail the relative stabilities and metal–carbon bond lengths in a series of structurally related $\sigma$-arylnickel complexes.

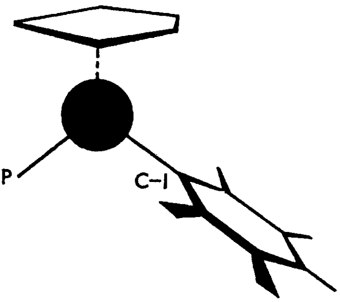
Treatment of $(\pi\text{-}C_5H_5)(Ph_3P)NiCl$ [9] with the appropriate aryl-lithium reagent[6,10] in diethyl ether at low temperatures, followed by hydrolysis and chromatography, has produced the following compounds in good yields: $(\pi\text{-}C_5H_5)(Ph_3P)Ni(\sigma\text{-}C_6H_5)$ (I);[11] $(\pi\text{-}C_5H_5)(Ph_3P)Ni(\sigma\text{-}C_6F_5)$ (II); $(\pi\text{-}C_5H_5)(Ph_3P)Ni(\sigma\text{-}C_6Cl_5)$ (III). Each of these complexes has been fully characterized by elemental analysis, molecular-weight measurement, and infrared and $^1H$ n.m.r. spectroscopy. All three compounds appear to be stable indefinitely in air at room temperature. On heating to 100° under a nitrogen atmosphere, the phenyl derivative (I) decomposes within several hours, whereas the perhalogenated complexes (II) and (III) appear to be stable for weeks. Moreover, complex (I) exhibits a noticeably decreased stability in organic solvents, and in the presence of 10% hydrochloric acid, as compared with (II) and (III). Crystals of the three species are not isomorphous. Pertinent data are:

$(\pi\text{-}C_5H_5)(Ph_3P)Ni(\sigma\text{-}C_6H_5)$ (I): space group $B2_1/c$ (No. 14), $a = 27{\cdot}42$, $b = 9{\cdot}49$, $c = 18{\cdot}25$ Å, $\beta = 102{\cdot}6°$, $Z = 8$, $D_m = 1{\cdot}28 \pm 0{\cdot}05$, $D_c = 1{\cdot}33$ g. cm.$^{-3}$;

$(\pi\text{-}C_5H_5)(Ph_3P)Ni(\sigma\text{-}C_6F_5)$ (II): space group $Pca2_1$ (No. 29), $a = 15{\cdot}15$, $b = 8{\cdot}91$, $c = 17{\cdot}85$ Å, $Z = 4$, $D_m = 1{\cdot}49 \pm 0{\cdot}05$, $D_c = 1{\cdot}52$ g. cm.$^{-3}$;

$(\pi\text{-}C_5H_5)(Ph_3P)Ni(\sigma\text{-}C_6Cl_5)$ (III): space group $P2_1/n$ (No. 14), $a = 9{\cdot}41$, $b = 15{\cdot}80$, $c = 18{\cdot}36$ Å, $\beta = 100{\cdot}7°$, $Z = 4$, $D_m = 1{\cdot}57 \pm 0{\cdot}05$, $D_c = 1{\cdot}57$ g. cm.$^{-3}$.

Single-crystal $X$-ray analyses of (I) and (II) have been undertaken using complete three-dimensional data collected with a Buerger Automated Diffractometer. Present discrepancy indices are: $R = 9{\cdot}2\%$ with 2400 reflections for (I) and $R = 10{\cdot}2\%$ with 1900 reflections for (II). The co-ordination geometry of the nickel is similar in the two complexes, and is shown in the Figure.



FIGURE

Nickel–phosphorus bond lengths are: $2{\cdot}133 \pm 0{\cdot}005$ Å in (I) and $2{\cdot}145 \pm 0{\cdot}004$ Å in (II). The $\sigma$-bonded aromatic system is approximately perpendicular to the P–Ni–C(1) plane [the actual dihedral angles are 102·4° in (I) and 100·3° in (II)]; this effect is presumably to maximize $d_\pi$–$p_\pi$ back-donation from the nickel into the aromatic system.

Surprisingly, the Ni–C(1) distances in the two complexes are indistinguishable within experimental error: $Ni\text{–}C_6H_5 = 1{\cdot}919 \pm 0{\cdot}013$ Å, $Ni\text{–}C_6F_5 = 1{\cdot}914 \pm 0{\cdot}014$ Å. Thus, although we anticipate a shortening of the Ni–C(1) bond because of the higher inductive effect of the $C_6F_5$ ligand, the shortening detected by crystallographic methods is not statistically significant. A *rationale* is, however, available. The Ni–C($sp^2$) distances in these molecules are less than 0·1 Å longer than the Ni–C($sp$) bond length in $Ni(CO)_4$ ($1{\cdot}82 \pm 0{\cdot}01$ Å).[12] A comparison of the great differences in metal–carbonyl and metal–alkyl (bond order = 1·0) bond lengths for other metals {Mo–CO = 1·94 Å in $[NH_2{\cdot}(CH_2)_2{\cdot}NH{\cdot}(CH_2)_2{\cdot}NH_2]Mo(CO)_3$,[13] Mo–$CH_3$ = 2·38 Å in $[C_{10}H_8Mo(CO)_3{\cdot}CH_3]_2$;[14] Fe–CO = 1·78 Å in $C_{10}H_8Fe_2(CO)_5$,[15] Fe–$CH_2$ = 2·123 Å in $(OC)_2Fe(\pi\text{-}C_5H_4)CH_2Fe(CO)_4$[16]} indicates that the Ni–σ-aryl bond order in the present complexes is considerably greater than unity. The similarity in Ni–$C_6H_5$ and Ni–$C_6F_5$ bond lengths therefore indicates that, even in the non-fluorinated derivative, the nickel–carbon bond order is already sufficiently increased from unity that the bond length is relatively insensitive to small changes in bond order.† Our results are consistent with the Co–$C_6H_2(CH_3)_3$ bond distances of 1·96 ± 0·01 Å in $[Co^{II}(mesityl)_2(PEt_2Ph)_2]$,[17] which we believe has a significant contribution from $d_\pi$–$p_\pi$ back-donation {*cf.*, the $Co^{II}$–$CH_3$ distance of 2·14 Å estimated from $r(Csp^3) = 0{\cdot}77$ Å and half the Co–Co distance of 2·736 Å in the non-bridged complex $[Co^{II}_2(CNMe)_{10}{}^{4+}]$}.[18]

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† See Figure 2 of ref. 13 for a plot of bond length against bond order for the Mo–C system.

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