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PREFERRED CONFORMATIONS IN TRANSITION METAL ALKYL COMPOUNDS

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SUMMARY

Compounds of the type π-$C_5H_5NiPPh_3CH_2R$ (R=alkyl, aryl) exhibit temperature-dependent ^1H NMR spectra because of hindered rotation about the nickel–carbon bond. Evidence is also presented which suggests that, at room temperature, compounds of the types π-$C_5H_5NiPPh_3CHR_2$, π-$C_5H_5FeCOPPh_3CH_2R$ and π-$C_5H_5RhBrPPh_3CH_2R$ exist almost exclusively in conformations in which the groups R are as far as possible from the cyclopentadienyl groups.

INTRODUCTION

As part of a systematic study of the chemical and physical properties of the homologous series of alkylnickel compounds π-$C_5H_5NiPPh_3R$ (R=C_1 to C_4 hydrocarbon radicals)[1], we have recently reported the ^{31}P NMR chemical shifts of these and related compounds[2]. Some vicinal coupling constants between the phosphorus nuclei and the protons on the carbon atoms bonded to the nickel are listed in Table 1. In most cases the data were obtainable only from the ^{31}P NMR spectra because the pertinent resonances in the proton spectra overlap considerably with other proton lines[1].

We had originally hoped that the magnitudes of the coupling constants would be dominated only by the Fermi contact term, and thus that the values of ^3J(PH) would be informative concerning the nature of the nickel–carbon bonds. The three-fold difference in ^3J(PH) on going from the methyl derivative to the secondary alkyl compounds, however, suggested strongly that other factors are also important, and it seemed likely that the differences arose from conformational effects.

Although rotation about a metal–carbon σ-bond is generally expected to be rapid on the NMR time scale at ambient temperatures, hindered rotation could result in more stable conformations (rotamers) being more highly populated than others. Thus the observed proton chemical shifts and coupling constants would be weighted averages of the chemical shifts and coupling constants of the individual conformations. By analogy with saturated organic systems[3], the vicinal phosphorus–hydrogen coupling constant should be a function of the dihedral angle, φ, between the

TABLE 1

VICINAL COUPLING CONSTANTS, ^3J(PNiCH), OF THE COMPOUNDS π-$C_5H_5NiPPh_3R$ IN CS_2 AT 25°C

R	*J(PH) (Hz)*
Me	5.6
Et	7.4
n-Pr	8.0
iso-Pr	18.0
n-Bu	8.0
iso-Bu	8.6
$PhCH_2$	8.8
sec-Bu	19.0
neopentyl	9.4
CH_2SiMe_3	9.8
$CH(Ph)(SiMe_3)$	16.8

PNiC plane and the NiCH plane. Thomas[4] has recently discussed the validity of the generally accepted equation developed by Karplus for organic systems[5]; it seems that the theory holds reasonably well for couplings between protons and ^{19}F, ^{13}C and ^{31}P. Recently it has been successfully applied to ^3J(POCH) of phosphate esters[6] and ^3J(PtNCH) of platinum(II) amino acid complexes[7]. In its simplest form the Karplus equation has the form:

$$^3J = K_1 \cos^2 \varphi + C \qquad 0 \leqslant \varphi \leqslant 90° \tag{1}$$

$$^3J = K_2 \cos^2 \varphi + C \qquad 90° \leqslant \varphi \leqslant 180° \tag{2}$$

where $C \lesssim 0$ and $K_2 \gtrsim K_1$. Consequently, vicinal coupling constants should be a minimum at $\varphi = 90°$ and a maximum for $\varphi = 0°$ (*cis*) and $\varphi = 180°$ (*trans*) with $J_{trans}(J_t) \gtrsim J_{cis}(J_c)$. Gauche conformations ($\varphi \approx 60°$ or 120°) have intermediate coupling constants (J_g).

RESULTS AND DISCUSSION

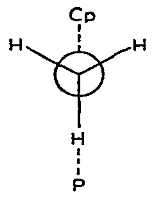
In the case of π-$C_5H_5NiPPh_3Me$, rotation about the nickel–carbon bond is rapid on the NMR time scale since only a single, averaged ^3J(PNiCH) coupling is observed. Because of the three-fold symmetry of the methyl group, $\langle \cos^2 \varphi \rangle = 0.5$, independent of conformation. If it is assumed that $K_2 \approx K_1$, *i.e.* $J_t \approx J_c$, then for the methyl compound,

$$\langle J \rangle = 0.5\, K_2 + C \tag{3}$$

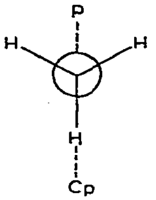
or, alternatively

$$\langle J \rangle = \frac{J_t + 2J_g}{3} \tag{4}$$

The former relationship follows from (1) and (2) while the latter can be derived by considering the conformations with eclipsed C–H bonds (I and II). The most important point concerning equation 3 is that it predicts that $\langle J \rangle$ is independent of conformation if $K_1 \approx K_2$.

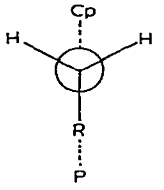


(I)



(II)

In the case of the primary alkyl compounds, the eclipsed conformations III and IV should be energetically unfavorable on steric grounds and one might anticipate that the favored conformations would be those with the R group tested away from the plane of Ni–P bond. Some possible conformations are shown below (it seems improbable that there will be specific conformations corresponding to distinct energy minima in this system). In V and VI, $\cos^2\varphi = 0.625$, $[(1+0.25)/2]$, while in VII, $\cos^2\varphi = 0.75$. Consequently an increase in ^3J(PNiCH) relative to the methyl compound would be expected. As shown in Table 1, this increase is actually observed, with ^3J(PNiCH) increasing with increasing bulk of R.



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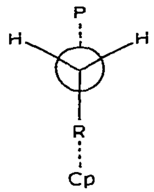

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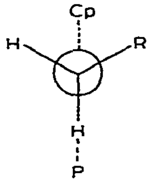

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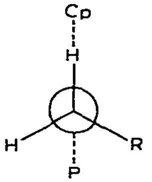

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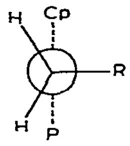

(VII)

If rotation through the barriers represented by conformations III and IV were slow on the NMR time scale, then the CH_2 spectrum should show non-equivalence of the methylene protons, *i.e.* an ABX pattern ($X = {}^{31}P$). Instead, an A_2X spectrum is noted in all cases, indicating rapid interconversion between conformations such as V–VII and the mirror image conformations with R on the other side of the P–Ni–Cp plane.

However, assuming that there is some steric hindrance to rotation, $\langle J \rangle$ should increase with decreasing temperature due to increasing population of conformations such as VII, and at sufficiently low temperature the A_2X spectrum should become an ABX spectrum.

Reliable variable temperature studies on most of the primary alkyl compounds in Table 1 were not possible because the proton spectra were complicated by overlap of the various resonances[1] and phosphorus NMR necessitated the use of 10 mm tubes, with the concomitant loss of resolution. The trimethylsilylmethyl derivative, however, is very stable and has the advantage that the methyl resonance at τ 10.19 is well separated from the methylene resonance at τ 11.31. Although the chemical shifts are only slightly solvent- and temperature-dependent, the coupling constant, ^3J(PH), and the methylene line widths do vary significantly with temperature. Figure 1 shows

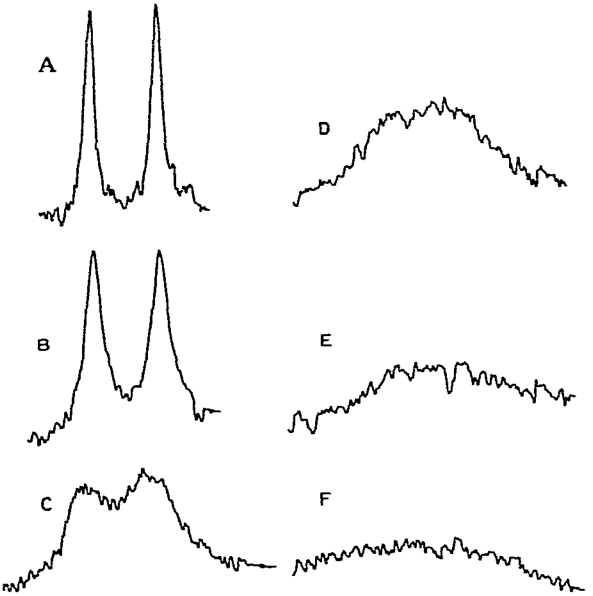

Fig. 1. NMR spectrum of the methylene resonance of π-$C_5H_5NiPPh_3CH_2SiMe_3$ at various temperatures: A, 298 K; B, 198 K; C, 168 K; D, 158 K; E, 143 K; F, 133 K.

the methylene doublet in the temperature range 133 K to 298 K. The lines broaden and diverge as the temperature is lowered, coalescing at about 150 K. The methylene resonance has virtually disappeared at 133 K, at which temperature the methyl singlet has only broadened slightly. Although no other resonances could be detected at this temperature, presumably rotation would be frozen out completely at lower temperatures and well-resolved lines corresponding to the stable conformations would appear as an ABX spectrum.

An approximate extrapolation to infinite temperature obtained by plotting ^3J(PH) against $1/T$ is shown in Fig. 2 and yields a coupling constant of 9.3 Hz. Presumably this is the average coupling constant of all conformations significantly populated at higher temperatures*.

In the case of the secondary alkyl compounds π-$C_5H_5NiPPh_3CHR_2$, a number of rotamers are possible, VIII-XIII.

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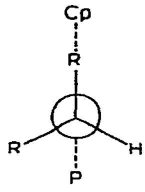
* This would not necessarily correspond to $\langle J \rangle$ at infinite temperature since certain conformations may not be populated at all over the temperature range studied.



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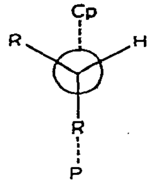

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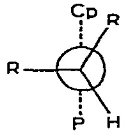

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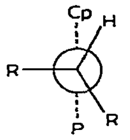

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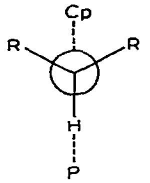

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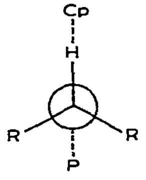

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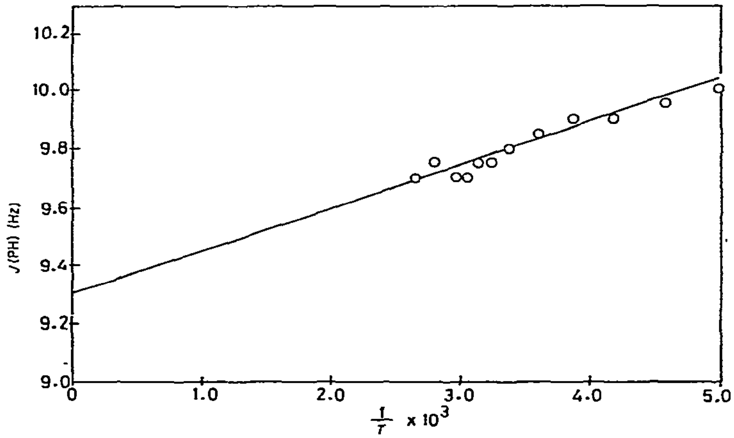


Fig. 2. Plot of $^3J(PH)$ of π-$C_5H_5NiPPh_3CH_2SiMe_3$ *vs.* $1/T$.

By analogy with the steric considerations presented for the primary alkyl compounds, conformations VIII–XI are expected to be of much higher energy than XII and XIII. The latter two conformations should have the largest coupling constants ($\varphi = 0°$, $180°$).

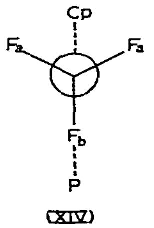
In order to study the temperature dependence of the NMR spectrum of a secondary alkyl derivative, the compound π-$C_5H_5NiPPh_3CH(Ph)(SiMe_3)$ was synthesized. The resonance of the methine proton appears at τ 9.51, well-separated from the methyl resonance at τ 10.22, and with a phosphorus-hydrogen coupling constant of 16.8 Hz. Although the methine doublet is broadened slightly at 153 K, the spectrum is little affected by variations in temperature, and the compound thus appears to exist almost exclusively as XII and/or XIII at room temperature. Since $^3J(PH)$ for the isopropyl and sec-butyl compounds are 18.0 and 19.0 Hz, respectively, they must also strongly favor XII and/or XIII at room temperature, and thus J_t for these systems is about 17–19 Hz.

Substituting $J_t = 18.0$ Hz into equation (4), J_g for the methyl compound is -0.6 Hz. From equation (3), $C = -6.8$ Hz and $K_2 = 24.8$ Hz.

Using these values for K_2 and C in equation (2) and again assuming $K_1 \approx K_2$ (for the primary alkyl compounds), for $\langle \cos^2 \varphi \rangle = 0.625$, $\langle {}^3J \rangle = 8.7$ and for $\langle \cos^2 \varphi \rangle = 0.75$, $\langle {}^3J \rangle = 11.8$. The former value corresponds to conformations V and VI while the latter corresponds to conformation VII. It is possible, in fact, that $K_2 > K_1$. Evidence is presented below which suggests that the cyclopentadienyl group has greater stereochemical requirements than does the triphenylphosphine. Consequently the secondary alkyl derivatives would prefer conformation XIII, with the result that the calculated values of $\langle J \rangle$ for the primary alkyl compounds would be somewhat smaller. Thus it is seen that the results for the primary alkyl compounds (Table 1) can be explained by assuming an increasing tendency for the R group to adopt a conformation at right angles to the ring with increasing bulk of R.

On the other hand, both J_g and J_t would be expected to vary somewhat with the substituents on the alkyl group, a complication which would depend on both bond lengths and bond angles and which is difficult to assess. By analogy with saturated organic systems[8], substitution of hydrogen or carbon by the less electronegative silicon on the carbon atom bonded to the nickel should increase ${}^3J$(PH). In agreement with this suggestion, ${}^3J$(PH) for $Ph_3PAuCH_2SiMe_3$ (10 Hz)[9], is about 2 Hz larger than ${}^3J$(PH) for Ph_3PAuMe (8 Hz)[10] or $Ph_3PAuCH_2CMe_3$ (8 Hz)[9]. Since π-$C_5H_5NiPPh_3CH_2CMe_3$ and π-$C_5H_5NiPPh_3CH_2SiMe_3$ have comparable vicinal coupling constants however (Table 1), it would seem that VII represents a definite energy minimum.

Suggestions may be made at this point concerning the relative effective sizes of the cyclopentadienyl and phosphine ligands. Churchill and O'Brien[11] have recently published the crystal structure of π-$C_5H_5NiPPh_3CF_3$. Although the complex exists in the crystal as two crystallographically independent molecules, its conformation is clearly XIV rather than XV, a fluorine eclipsing the phosphorus rather than the cyclopentadienyl group.



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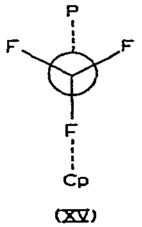
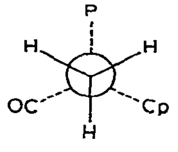


(XV)

Even so, the distances between the π-C_5H_5 group and the $C(F_a)_2$ group are close to the sums of the Van der Waals radii[12], while F_b lies much further from the triphenylphosphine atoms. A similar structure has been reported for π-$C_5H_5NiPPh_3$-$GeCl_3$[13], and thus the cyclopentadienyl group may well interact with bulkier groups than fluorine to a greater extent than the triphenylphosphine.

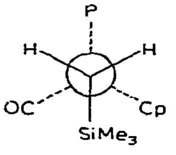
There are as yet very few examples in the literature where vicinal phosphorus–hydrogen coupling constants can be used to rationalize the presence and the structures of alkylmetal conformational isomers. The NMR spectrum of the methyl resonance of π-$C_5H_5FeCOPPh_3Me$ is a time-averaged doublet at room temperature with $^3J(PH) = 6.5$ Hz[14]. Only one conformation is possible, (XVI), (*cf.* the identical conformation in π-$C_5H_5FeCO[Ph_2P\underline{C{=}C(PPh_2)(CF_2)_2C}F_2]SnMe_3$[15]).



(XVI)

The methylene resonance in the NMR spectrum of π-$C_5H_5FeCOPPh_3CH_2$-$SiMe_3$ is reported to be the AB part of an ABX system[16], with vicinal phosphorus–hydrogen coupling constants of 2 Hz and 13 Hz. Although the asymmetry about the iron atom would make the methylene protons formally non-equivalent in any case, the large difference in vicinal coupling constants implies a definite preference for a conformation with one *trans* and one *gauche* phosphorus–hydrogen coupling constant.

Although no attempt was made[16] to assign the methylene resonances, three staggered conformations are possible, XVII, XVIII and XIX.



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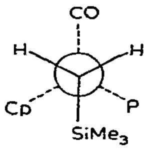

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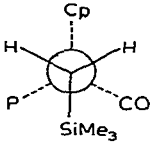


(XIX)

Both hydrogen atoms are *gauche* to the phosphine in XVII, and thus both would exhibit small, almost equal phosphorus–hydrogen coupling constants. Conformations XVIII and XIX, on the other hand, should both exhibit a large (J_t) and a relatively small (J_g) coupling constant, as is indeed the case. Thus the preferred conformation in solution must be either XVIII or XIX.

In XIX the bulky trimethylsilyl group is *gauche* to a CO and a triphenylphosphine group, in XVII it is *gauche* to a CO and a cyclopentadienyl group. XVII has already been ruled out as the most stable conformation. Making the reasonable assumption that the CO is the least bulky of the three groups, it follows logically that (1) XIX is more stable than XVIII and is consequently the most stable conformation; (2) the cyclopentadienyl group causes greater steric hindrance than the triphenylphosphine group in this system (otherwise XVII would be most stable). The latter conclusion is in agreement with the conclusion reached above for the nickel complexes. While XIX is preferred, this does not rule out the presence of smaller populations of conformations XVIII and XVII.

The methylene resonance of the compound π-$C_5H_5FeCOPPh_3CH_2Ph$ is also reported to be the AB part of an ABX system[17], although the coupling constants were not given. They are obviously quite different, however, indicating that while rotation about the iron–carbon bond is probably rapid on the NMR time scale, there is a strongly preferred conformation. It should be noted that these NMR data are consistent with recent reports of rotational isomerism as indicated by the infrared spectra of a number of related iron carbonyl complexes[18].

The methylene resonance of the compound π-$C_5H_5RhPPh_3CH_2PhBr$[19] also shows unequal couplings to the phosphorus, in this case 3.8 Hz and 12.0 Hz. Again a preferred conformation with one hydrogen *gauche*, the other *trans*, is indicated.

In an effort to study a compound with an intermediate rate of rotation about a metal–carbon bond, the compounds π-$C_5H_5FeCOPPh_3Et$[20] and π-$C_5H_5FeCOPPh_3CF_3$[21] were prepared. The former compound was found to be unsuitable for study because the methyl and methylene resonances overlapped considerably in the proton NMR spectrum and the phosphorus NMR spectrum was not satisfactorily resolved.

The room temperature ^{19}F resonance of the trifluoromethyl compound in 1/1 CH_2Cl_2–$CFCl_3$ consisted of a doublet at 13.5 ppm downfield from $CFCl_3$, $^3J(PF) = 2.9$ Hz. Both the chemical shift and the coupling constant vary with temperature, the former by about 0.5 ppm in the temperature range 160–300 K. The spectrum in the temperature range 163–303 K is shown in Fig. 3. The coupling constant decreases with decreasing temperature, the rate of decrease being somewhat solvent dependent, and the coalescence temperature is approximately 250 K in 1/1 CH_2Cl_2–$CFCl_3$. Extrapolations of $^3J(PF)$ to infinite temperature as in Fig. 2 yield limiting coupling constants of 6.4 Hz in 1/1 CH_2Cl_2–$CFCl_3$ and 10.5 Hz in 3/1 C_6H_6–$CFCl_3$. These

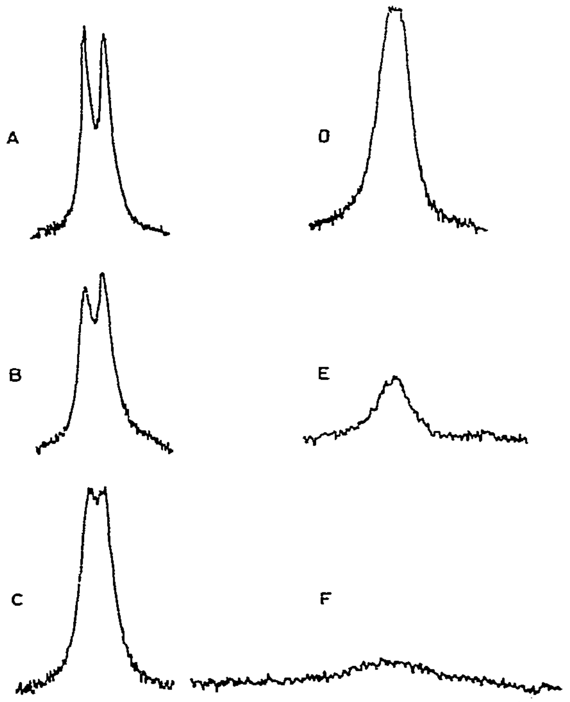
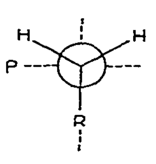


Fig. 3. ^{19}F NMR spectrum of π-$C_5H_5FeCOPPh_3CF_3$ at various temperatures: A, 303 K; B, 273 K; C, 263 K; D, 243 K; E, 173 K; F, 163 K.

results may indicate that the ^{31}P–^{19}F coupling constants are solvent and temperature dependent even in the individual conformations.

Although no other lines appeared at 163 K, lower temperatures would presumably slow rotation down sufficiently that separate fluorine resonances would be observed. Experiments are currently underway to achieve this by using bulkier phosphines and perfluoroalkyl derivatives. It has been reported that the fluorine resonances of the compounds π-$C_5H_5RhPPh_3R_FX$ ($R_F = C_2F_4Br$, C_2F_4H, C_3F_7; X = Br; I) are very broad[19], and it is interesting to speculate about the possible effects that varying the temperature would have on the spectra of these compounds.

Our results show quite clearly that preferred conformations for rotation about metal–carbon bonds in complexes strongly affect the nature of the observed NMR spectra. ^{31}P–H coupling constants can be used to deduce the preferred conformation(s) in many cases. As well as in the pseudotetrahedral and pseudotrigonal cases discussed here, conformational effects can also be expected to occur in octahedral complexes when the coordinated alkyl group is *cis* to the vicinal phosphine, (XX and XXI represent possible conformations) although not when *trans*.



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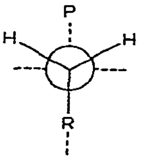

(XXI)

A number of complexes are known in which methyl groups *cis* and *trans* to tertiary phosphines exhibit different phosphorus–hydrogen coupling constants[22–26]. In some cases, it has been assumed that $J_{cis} < J_{trans}$ when making assignments. Our work suggests that *cis* coupling constants of substituted methyl compounds may be strongly temperature dependent, and that the importance of conformational effects should not be overlooked.

EXPERIMENTAL

The iron compounds, π-$C_5H_5FeCOPPh_3R$ (R = Et[20], CF_3[21]) were prepared as in the literature. The nickel compounds, π-$C_5H_5NiPPh_3R$ ($R = CH_2SiMe_3$, $CHPhSiMe_3$) are new compounds and were prepared from π-$C_5H_5NiPPh_3Cl$ and the appropriate Grignard reagent[1]. The former is a stable green, crystalline compound, m.p. 130–131°C (sealed tube). (Found: C, 68.53; H. 6.79. $C_{27}H_{31}NiPSi$ calcd.: C, 68.80; H, 6.50%.)

The secondary alkyl derivative is a stable, red-brown crystalline compound, m.p. 112–113°C (sealed tube). (Found: C, 71.97; H, 6.51. $C_{33}H_{35}NiPSi$ calcd.: C, 72.14; H, 6.42%.)

The NMR spectra were run on a Bruker HX-60 spectrometer with internal lock. The low temperature ^{19}F spectra of π-$C_5H_5FeCOPPh_3CF_3$ were run in 1/1 CH_2Cl_2–$CFCl_3$ and were locked on the fluorine resonance of $CFCl_3$. High temperature spectra of this compound were run in 3/1 C_6H_6–$CFCl_3$, locked again on $CFCl_3$. The low temperature spectra of π-$C_5H_5NiPPh_3CH_2SiMe_3$ and π-$C_5H_5NiPPh_3CHPhSiMe_3$

were run in $CHFCl_2$ and were locked on the high-field proton line of the solvent. The high temperature spectra of these two nickel compounds were run in toluene (locked on methyl line of the solvent) and benzene (locked on benzene line), respectively.

ACKNOWLEDGEMENTS

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