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A VERY LOW-FIELD AROMATIC PROTON RESONANCE IN THE PMR SPECTRUM OF A CONFORMATIONALLY CONSTRAINED ARYLNICKEL COMPLEX

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SUMMARY

The ^1H NMR spectrum of 2,2′-bis[chlorobis(triethylphosphine)nickel]-biphenyl, (I), exhibits the H_6 and $H_{6'}$ resonance at δ 12.00 ppm in $CDCl_3$ (12.27 in C_6D_6), 4.4 ppm downfield from the resonance of the corresponding protons in biphenyl. The large downfield shift is attributed to static very-short distances of H_6 and $H_{6'}$ to nickel atoms in (I) that are enforced by its sterically-fixed conformation.

INTRODUCTION

Hydrocarbon ligand protons situated above or below the bonding plane in square-planar nickel and palladium complexes and near the metal atom resonate at 0.5 to 3.3 ppm lower field than the resonances for the same protons in more conventional environments[1-4]. A somewhat similar phenomenon occurs in arylcopper[5] and aryllithium[6,7] compounds where downfield shifts as large as 1.5 ppm for the *ortho* protons were observed. In contrast, upfield shifts of 3–4 ppm were found for ligand protons near the metal in certain molybdenum complexes[8], while both an upfield and a downfield shift were observed for different protons in the NMR spectrum of *o*-anisylcopper[5]. These shifts have been attributed to an induced anisotropic paramagnetic contribution to the molecular susceptibility centered at the metal atom[3,9], between a carbon–metal bond[5], or at a carbon bonded to the metal[6,7]. An interaction (possibly bonding) between the affected proton and the metal has also been suggested as the origin of the shifts[4,8]. In the first-mentioned theory, the magnitude of the shift is predicted to become greater the closer the protons approach the metal[3,9]. To further evaluate this prediction, 2,2′-bis[chlorobis(triethylphosphine)nickel]biphenyl, (I), was synthesized for NMR study. This complex is of interest since very short non-variable distances from the nickel atoms to ligand protons H_6 and $H_{6'}$ are sterically enforced.

RESULTS AND DISCUSSION

Complex (I), dec. 137–140°, was the only product isolated when $NiCl_2(PEt_3)_2$ was treated with 2,2′-dilithiobiphenyl. The general procedure is the same as that used

TABLE 1

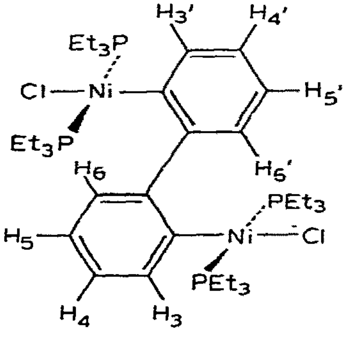
AROMATIC PROTON CHEMICAL SHIFTS (δ, ppm) OF (I), (II), AND BIPHENYL

Compound	*Solvent*	H_2	$H_{2'}$	$H_{6'}$	H_6	H_3	$H_{3'}$	$H_{5,5'}$	$H_{4,4'}$
(I)	$CDCl_3$			12.00	12.00	8.02	8.02	——6.7–7.3——	
(I)	C_6D_6			12.27	12.27	8.15	8.15	——6.7–7.3——	
(II)	$CDCl_3$		9.09	9.09	——6.7–7.7——				
Biphenyl[a]	$CDCl_3$	7.58	7.58	7.58	7.58	7.42	7.42	7.42	7.32

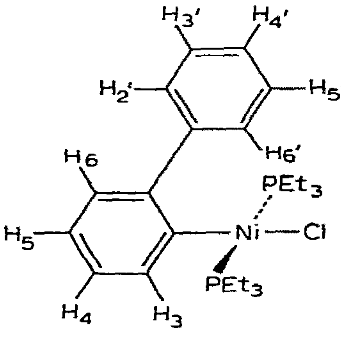
[a] Ref. 13.

by Chatt and Shaw for the synthesis of mononuclear organonickel derivatives[10]. An oxidative addition[11] of 2,2'-dibromobiphenyl to $Ni(1,5\text{-}COD)(PEt_3)_2$ followed by chloride for bromide metathesis afforded (I) with a higher decomposition point, 156–159°, but the yield was very low and several by-products were formed. The major identified product from the reaction, complex (II), was isolated in 8% yield.

Assignments for the aromatic proton resonances of (I), (II), and biphenyl are given in Table 1. In $CDCl_3$, where sample decomposition slowly takes place[3,12]; the resonance for H_6 and $H_{6'}$ of (I) is a partially broadened doublet (J 8 Hz) at δ 12.00 ppm. This resonance is 4.4 ppm downfield from the resonance of the corresponding protons in biphenyl.



(I)



(II)

In C_6D_6, the spectrum of (I) is better resolved (Fig. 1), and the H_6 and $H_{6'}$ resonance is shifted to δ12.27 ppm. The H_3 and $H_{3'}$ resonance appears as a doublet (J 8 Hz) at δ8.02 ppm in $CDCl_3$, while the remaining aromatic proton resonances are, in fact, shifted very slightly upfield from the corresponding biphenyl proton resonances. Slight upfield shifts for *meta* and *para* protons have been observed in other aryl metal compounds[3,5]. A downfield shift is also observed in the spectrum of (II) as the doublet resonance for $H_{2'}$ and $H_{6'}$ occurs at δ9.09 ppm, but the shift is only 1.5 ppm from the resonance of the corresponding protons in biphenyl.

Molecular models indicate that (I) is locked, due to steric congestion, in an *anti* conformation with a phenyl–phenyl dihedral angle of *ca.* 35°. In addition to enforcing the *anti* conformation by mutual steric repulsion, the nickel substituents exert a steric force against the H_6 and $H_{6'}$ protons which may be partially relieved only by increasing the C_1–C_2–Ni and $C_{1'}$–$C_{2'}$–Ni angles, the C_1–C_6–H_6 and $C_{1'}$–$C_{6'}$–

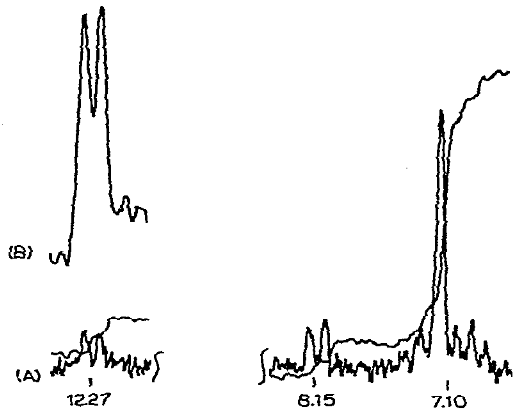


Fig. 1. (A), ^{1}H NMR spectrum of the phenyl protons of (I) in C_6D_6. The intense resonance at δ7.15 ppm is due to ^{1}H impurities in the solvent. (B), the δ12.27 ppm resonance at increased spectrum amplitude.

$H_{6'}$ angles, and/or by lengthening the C_1–$C_{1'}$ bond. In the absence of these distortions, the H_6 to nickel distance is estimated to be *ca.* 2.2 Å, assuming a C–Ni bond length of 1.91 Å. In other complexes exhibiting unusual chemical shifts, CH—Pd and CH—Mo distances were estimated to be 2.3 Å[4] and 2.5 Å[8], respectively. A BH—Mo distance of 2.15 Å (avg. distance of two enantiomorphs) has been taken as evidence for a three-center B–H–Mo bond[14]. In complex (II), the resonance for $H_{2'}$ and $H_{6'}$ is shifted only slightly downfield. Here, molecular conformations other than those of closest $H_{2'}$ or $H_{6'}$ to nickel approach are accessible by allowed rotations about the phenyl–phenyl bond.

EXPERIMENTAL

Reactions were conducted under a nitrogen atmosphere and in predried solvents and glassware. 2,2'-Dilithiobiphenyl[15] and Ni(1,5-COD)$_2$[16] were prepared by published procedures. Column chromatography was performed on Baker acid-washed alumina where chloride for bromide metathesis on nickel is known to occur[17]. NMR spectra were recorded on a Varian T-60 spectrometer and are referenced to internal tetramethylsilane. Integrated peak areas for (I) and (II) were in agreement with the proposed structures.

Synthesis of (I) by the organolithium method

A solution of 1.00 g (2.7 mmol) of $NiCl_2(PEt_3)_2$ in 10 ml of ether was treated with 30 ml of a *ca.* 0.045 molar solution of 2,2'-dilithiobiphenyl in ether. After stirring the solution for 1 h at 25°, it was washed with 25 ml of aqueous NH_4Cl at 0° and diluted with 20 ml of pentane. The solution was dried over $MgSO_4$ and filtered through acid-washed alumina. Evaporation of the filtrate, under vacuum, to a red-brown oil followed by crystallization from CH_3OH/H_2O and then recrystallization from pentane yielded 0.118 g (11%) of (I): m.p. 136–139° dec. (Found: Cl, 8.6. $C_{36}H_{68}$-$Cl_2Ni_2P_4$ calcd.: C, 53.18; H, 8.43; Cl, 8.72%.) A sample of (I) prepared earlier by the same procedure was analyzed for C, H (found: C, 53.2; H, 8.3%). IR (Nujol): 3030 w, 1565 w, 1555 vw, 1420 w, 1410 w, 1400 w, 1365 w, 1255 w, 1240 w, 1158 vw, 1037 s, 1015 w, 767 m, 759 w, 740 s, 725 w, and 700 vw cm^{-1}.

Synthesis of (I) and (II) by oxidative addition

A solution of Ni(1.5-COD)$(PEt_3)_2$, prepared by stirring 8 mmol of Ni(1,5-COD$)_2$ with 19 mmol of PEt_3 in 10 ml of benzene[18], was treated with 6.4 mmol 2,2'-dibromobiphenyl in benzene. After 2 h, the solution was filtered. The filtrate was washed with aqueous NH_4Cl at 0°, dried over $MgSO_4$, and concentrated to a red oil under vacuum. A pentane extract of the oil was concentrated and stored at $-20°$ for 72 h. Filtration of the extract yielded 0.10 g (3%) of $NiBr_2(PEt_3)_2$. The filtrate was then chromatographed on acid-washed alumina. Elution with 20/50/30 ether/pentane/benzene afforded, after recrystallization from pentane, 0.24 g (8%) of (II): m.p. 98–100°. (Found: C, 59.0; H, 8.1. $C_{36}H_{39}ClNiP_2$ calcd.: C, 59.60; H, 8.13%.) IR (Nujol): similar to that of (I) except between 670–800 cm^{-1} where absorptions occur at 766 m, 743 s, 734 w, 721 w, and 697 m cm^{-1}. Elution with 70/30 ether/pentane yielded, after recrystallization from benzene/pentane, 0.07 g (2%) of (I): m.p. 156–159° dec. (Found: C, 53.3; H, 8.2%.) IR (Nujol): identical to that described above for (I). Continued development of the column with increasing proportions of CH_3OH in ether eluted a trace amount of a red compound thought to be $NiCl_2(PEt_3)_2$ followed by an unidentified water-soluble yellow compound.

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