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Perhaloarylmetal Chemistry. IV. Formation and Properties of Some Organonickel Derivatives of the Type $(\pi\text{-}C_5H_5)(R_2R'P)(R'')Ni$[1,2]

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A series of air-stable organonickel complexes of the type $(\pi\text{-}C_5H_5)(R_2R'P)(R'')Ni$ (R = phenyl, R′ = methyl or phenyl, and R″ = methyl, phenyl, or perhalophenyl) containing σ-bonded organic substituents has been obtained from organonickel halides $(\pi\text{-}C_5H_5)(R_2R'P)NiCl$ and appropriate organolithium reagents. Analogous trifluoromethyl and heptafluoropropyl derivatives have been prepared from reactions of the respective perfluoroalkyl iodides with bis(π-cyclopentadienyl)dicarbonyldinickel followed by treatment with triphenylphosphine. The perhalogenated derivatives have been found to exhibit enhanced thermal, oxidative, and hydrolytic stabilities compared to their hydrocarbon analogs. σ-Bonded methyl complexes of this series readily undergo insertion with sulfur dioxide to form S-methylsulfinato derivatives. Trends in the proton nmr spectra of these σ-bonded organonickel complexes are discussed.

In conjunction with our continuing program on σ-bonded perhaloaryl derivatives of the transition metals, it was of interest to investigate the formation and properties of corresponding analogs of nickel. Perhaloarylnickel derivatives of the type $(R_3P)_2(R')NiX$ ($R' = C_6Cl_5$ or C_6F_5[3–5]) and $(R_3P)_2(R')_2Ni$ ($R' = C_6F_5$[5]) have recently been described in the literature. It seemed reasonable that organonickel halides of the type $(\pi\text{-}C_5H_5)(R_2R'P)NiX$ would also serve as excellent starting materials, since reactions with perhalogenated organolithium reagents should lead to σ-bonded organic derivatives which would be stabilized by π-bonding tris(organophosphine) and π-cyclopentadienyl ligands as well as by the perhalogenated alkyl or aryl substituent. Early in our studies, Yamazaki and coworkers[6] independently found that stabilization in this organonickel system is such that even nonperhalogenated σ-alkyl and σ-aryl derivatives can be isolated and characterized. In this paper, we describe the synthesis, reactivity, spectral properties, and qualitative stabilities of a series of organonickel derivatives, $(\pi\text{-}C_5H_5)(R_2R'P)(R'')Ni$. In a subsequent paper, we will discuss in detail the relative thermal stabilities of these substances, and the products of their thermal decomposition as measured by a combination of thermal analysis–mass spectrometric techniques.[7]

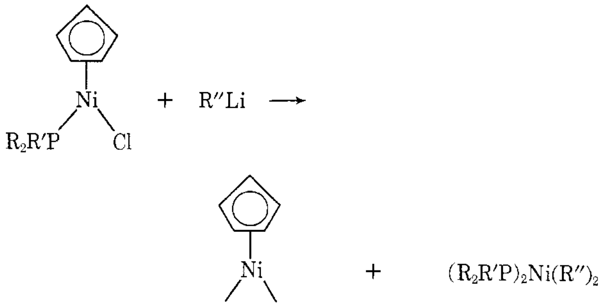
Organonickel halides of the type $(\pi\text{-}C_5H_5)(R_3P)NiX$ were first described in the literature in 1962 as a result of investigations of Schroll[8] and of Schropp.[9] Schroll's procedure, the most straightforward of the two methods, involved a disproportionation reaction between bis(triphenylphosphine)dichloronickel and nickelocene in a refluxing inert solvent to form π-cyclopentadienyl(triphenylphosphine)nickel chloride (**1**). We have successfully repeated this reaction using tetrahydrofuran as the solvent and have extended the procedure to include the diphenylmethylphosphine analog (**2**)

$$[R_2R'P]_2NiX_2 + (\pi\text{-}C_5H_5)_2Ni \longrightarrow 2(\pi\text{-}C_5H_5)(R_2R'P)NiX$$

1, R, R′ = C_6H_5; X = Cl
2, R = C_6H_5; R′ = CH_3; X = Cl

Yamazaki and coworkers[6] have also reported several additional examples of this type of disproportionation reaction, and it would appear that the procedure represents a general synthetic route to this class of organonickel halides. More recently, π-cyclopentadienyl(triphenylphosphine)nickel halides (X = Cl, Br, I) have been obtained in good yield from nickelocene and triphenylphosphonium halides.[10]

The reactions of organonickel halides **1** and **2** with organolithium reagents also appears to be a general process. Corresponding σ-bonded organic derivatives have been isolated in all experiments except those involving trichloromethyllithium. The latter is known to



3, R, R′ = C_6H_5; R″ = C_6F_5
5, R = C_6H_5; R′ = CH_3; R″ = C_6F_5
7, R, R′ = C_6H_5; R″ = C_6Cl_5
8, R = C_6H_5; R′ = CH_3; R″ = C_6Cl_5
9, R, R′ = C_6H_5; R″ = C_6H_5
10, R, R′ = C_6H_5; R″ = CH_3

4, R, R′ = C_6H_5; R″ = C_6F_5
6, R = C_6H_5; R′ = CH_3; R″ = C_6F_5

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[1] Part III: M. D. Rausch, T. R. Criswell, and A. K. Ignatowicz, *J. Organometal. Chem.* (Amsterdam), **13**, 419 (1968).

[2] Presented in part at the Second International Symposium on Organometallic Chemistry, Madison, Wis., Aug 30–Sept 3, 1965, and in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., March 31–April 5, 1968.

[3] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1718 (1960).

[4] J. R. Moss and B. L. Shaw, *ibid.*, *A*, 1793 (1966).

[5] J. R. Phillips, D. T. Rosevear, and F. G. A. Stone, *J. Organometal. Chem.* (Amsterdam), **2**, 455 (1964).

[6] H. Yamazaki and N. Hagihara, *Bull. Chem. Soc. Japan*, **37**, 907 (1964); H. Yamazaki, T. Nishido, Y. Matsumoto, S. Sumida, and N. Hagihara, *J. Organometal. Chem.* (Amsterdam), **6**, 86 (1966).

[7] H. G. Langer, T. Brady, H. B. Gordon, and M. D. Rausch, in preparation.

[8] G. E. Schroll, U. S. Patent 3,054,815 (1962); *Chem. Abstr.*, **58**, 1494*c* (1963).

[9] W. K. Schropp, *J. Inorg. Nucl. Chem.*, **24**, 1690 (1962).

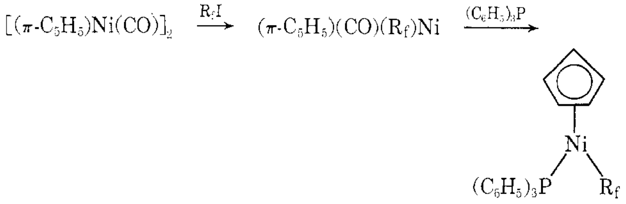
[10] M. Van den Akker and F. Jellinek, *Rec. Trav. Chim.*, **86**, 897 (1967).

be unstable above *ca.* −100°,[11] and the reagent may have possibly decomposed before reaction with **1** occurred. Our initial studies involved the reaction of pentafluorophenyllithium[12] and **1**. The expected pentafluorophenyl derivative **3** was obtained in 81% yield, as well as a second product (4% yield) which was shown to be bis(triphenylphosphine)bis(σ-pentafluorophenyl)nickel (**4**) by comparison with an authentic sample prepared by the method of Stone, *et al.*[5]

A similar reaction between **2** and pentafluorophenyllithium afforded a 73% yield of the pentafluorophenyl derivative **5** and a 4% yield of bis(diphenylmethylphosphine)bis(σ-pentafluorophenyl)nickel (**6**). The structure of the latter complex was likewise confirmed by its synthesis directly from bis(diphenylmethylphosphine)dichloronickel and an excess of pentafluorophenyllithium.[13] The mechanism for the formation of the bis(tris(organophosphine))nickel products **4** and **6** is presently obscure and is under further investigation.

Analogous reactions of pentachlorophenyl-,[14] phenyl-, and methyllithium with the appropriate organonickel halide **1** or **2** readily produced the corresponding σ-bonded pentachlorophenyl (**7**, **8**), phenyl (**9**), and methyl (**10**) analogs. In none of these reactions was the corresponding $(R_2R'P)_2Ni(R'')_2$ complex isolated. Such a result is not surprising, however, since complexes of the type $(R_2R'P)_2Ni(R'')_2$, where $R'' = C_6H_5$ or CH_3, are known to be unstable thermally[3] and would not have survived work-up of the products, while analogous complexes where $R'' = C_6Cl_5$ are known to be formed with extreme difficulty, owing to steric factors associated with the bulky *o*-Cl atoms.[13] The methyl and phenyl derivatives **9** and **10** have been independently prepared by Yamazaki, *et al.*,[6] *via* **1** and appropriate Grignard reagents.

In connection with our thermal stability studies,[7] it was imperative to have available $(\pi\text{-}C_5H_5)(R_2R'P)(R'')Ni$ complexes in which R'' is a perfluoroalkyl substituent. Since techniques for the formation of perfluoroalkyllithium and Grignard reagents have not yet been developed to the point where these reagents are generally useful in organometallic synthesis, the above approach did not seem promising. We turned instead to an extension of earlier work by Stone, *et al.*[15] These investigators have shown that reactions of bis(π-cyclopentadienyl)dicarbonyldinickel and perfluoroalkyl iodides produce deep red, air-stable liquids of the type $(\pi\text{-}C_5H_5)(CO)(R_f)Ni$. In the case of the pentafluoroethyl analog, carbon monoxide could be readily displaced to afford the corresponding complex $(\pi\text{-}C_5H_5)[(C_6H_5)_3P](C_2F_5)Ni$. In a similar manner, we have been able to prepare the corresponding trifluoromethyl (**11**) and heptafluoropropyl (**12**) analogs.



11, $R_f = CF_3$
12, $R_f = C_3F_7$

All of the $(\pi\text{-}C_5H_5)(R_2R'P)(R'')Ni$ complexes prepared in our studies occur as dark green crystals and are stable in air at ambient temperatures. The perhaloaryl and perfluoroalkyl derivatives **3**, **5**, **7**, **8**, **11**, and **12** are apparently indefinitely stable under these conditions. No detectable decomposition of the phenyl and methyl analogs **9** and **10** was noted when these complexes were exposed to air for periods of several weeks. However, crystals of **9** and **10** which had been exposed to air for 6 months or more gradually lost their dark green color, and this process was accompanied by the formation of a yellowish white solid. When a sample of **9** was heated to 100° under a nitrogen atmosphere, extensive decomposition occurred in a matter of several hours, whereas the corresponding perhalogenated complexes **3** and **5** were stable for weeks at this temperature. Moreover, solutions of **9** and **10** were exceedingly more air sensitive than were solutions of their perhalogenated analogs. These trends in relative stability are in keeping with earlier findings in which transition metal–perhaloaryls and –perhaloalkyls were found to exhibit considerably enhanced thermal and oxidative stabilities compared to their hydrocarbon analogs.[1,16–18] The reasons for these stability trends are still not completely clear; however, it is interesting to note that the carbon–nickel bond lengths in both the σ-bonded phenyl and pentafluorophenyl complexes **9** and **3** are indistinguishable within experimental error.[19] We hope to gain a better understanding of the factors affecting the relative stabilities of σ-bonded organic derivatives of transition metals by a combination of thermal and X-ray crystallographic analysis studies which are in progress.

In order to compare the hydrolytic stability of σ-perhaloaryl derivatives of nickel with their hydrocarbon counterparts, we have briefly studied the hydrolyses of these compounds under both heterogeneous and homogeneous conditions. In heterogeneous hydrolysis, each compound was mixed with water, 10% sodium hydroxide, or 10% hydrochloric acid, and the mixture was heated to reflux for 3 hr. In homogeneous hydrolysis, each compound was first dissolved in tetrahydrofuran and then mixed with either 10% sodium hydroxide or 10% hydrochloric acid and the solution was heated to reflux for 3 hr. In each experiment, the mixture was allowed to cool to room temperature, the starting material (if any) was recovered and identified, and the aque-

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[11] G. Kobrich, K. Flory, and R. H. Fischer, *Chem. Ber.*, **99**, 1793 (1966); D. F. Hoeg, D. I. Lusk, and A. L. Crumbliss, *J. Am. Chem. Soc.*, **87**, 4147 (1965).

[12] P. L. Coe, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 3227 (1962).

[13] F. E. Tibbetts and M. D. Rausch, unpublished studies.

[14] M. D. Rausch, F. E. Tibbetts, and H. B. Gordon, *J. Organometal. Chem.* (Amsterdam), **5**, 493 (1966).

[15] D. W. McBride, E. Dudek, and F. G. A. Stone, *J. Chem. Soc.*, 1752 (1964).

[16] P. M. Treichel and F. G. A. Stone, *Advan. Organometal. Chem.*, **1**, 143 (1964).

[17] M. D. Rausch, *Trans. N. Y. Acad. Sci.*, **28**, 611 (1966).

[18] R. D. Chambers and T. Chivers, *Organometal. Chem. Rev.*, **1**, 278 (1966).

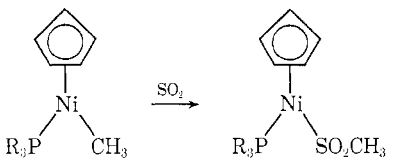
[19] M. R. Churchill, T. A. O'Brien, M. D. Rausch, and Y. F. Chang, *Chem. Commun.*, 992 (1967).

ous layer was analyzed by the dimethylglyoxime nickel test.

In the heterogeneous hydrolyses, all the organonickel compounds were stable to both water and 10% sodium hydroxide. In 10% hydrochloric acid, however, the compounds were appreciably less stable; for instance, **9** and **10** were completely decomposed, while **3** and **7** were only slightly decomposed. In homogeneous hydrolyses, all of the complexes were found to be unstable to 10% hydrochloric acid. The tetrahydrofuran solutions of **9** and **10** containing acid decomposed immediately after refluxing was initiated, but the solutions of **3** and **7** remained unchanged for *ca.* 15 min after the initiation of refluxing. Tetrahydrofuran solutions of all of the organonickel complexes were relatively stable to hydrolysis by 10% sodium hydroxide, and only partial decomposition was observed for each compound, although decomposition was again more extensive for the hydrocarbon analogs **9** and **10**.

An important feature of σ-bonded organic transition metal compounds has been their ability to undergo a variety of insertion reactions. Booth and Chatt[20] have recently found that solutions of the complexes *trans*-$[(C_2H_5)_3P]_2Pd(CH_3)X$ (X = Cl or Br), which do not contain carbon monoxide as a ligand, absorb 1 mol of carbon monoxide at atmospheric pressure and temperature to form the acetylated products *trans*-$[(C_2H_5)_3P]_2Pd(COCH_3)X$. The analogous platinum complexes also carbonylated, although more forcing conditions were required. The use of triphenylphosphine as a ligand in the palladium series was found to give less stable acetyl complexes. In view of these findings, we attempted the carbonylation of the methyl derivatives **10** and **13** under a variety of conditions. When carbon monoxide was bubbled through solutions of either **10** or **13** at room temperature or below, no acetylated products could be detected. In experiments in which an ethyl ether solution of **10** was saturated with carbon monoxide and was heated in a pressure bottle at 45° for 1 hr, a greenish brown oil resulted whose infrared spectrum indicated weak absorption in the expected carbonyl region near 1650 cm^{-1}. Attempts to isolate an acetylated product, however, were unsuccessful. Analogous attempted carbonylations of **13** generally led to undefined products containing absorption bands in the terminal carbonyl region. In this connection, it is interesting to note that Yamazaki and coworkers[6] observed that the reaction of either **9** or **10** with carbon monoxide at high pressure also failed to give acylated products, the main product being triphenylphosphinetricarbonylnickel. It thus appears that carbon monoxide does not readily insert into carbon–nickel bonds in the above series of organonickel complexes.

Insertion reactions involving sulfur dioxide have proved to be considerably more successful. Wojcicki and coworkers[21] have recently reported that a variety of σ-bonded organic derivatives of iron, manganese, and rhenium react with liquid sulfur dioxide with formation of corresponding S-sulfinato complexes. On the basis of spectral data, these complexes have been assigned structures containing $M-S(O)_2-R$ linkages. We have now found that the methyl derivatives **10** and **13** are also readily converted to their corresponding S-sulfinato derivatives **14** and **15** by reaction with sulfur dioxide at low temperatures, and these findings represent the first examples of sulfur dioxide insertion into a carbon–nickel bond. The insertion products **14** and **15** were characterized by elemental analysis as well as by their infrared and nmr spectra.



10, R = C_6H_5
13, R = n-C_4H_9

14, R = C_6H_5
15, R = n-C_4H_9

The proton nmr spectra of all the $(\pi\text{-}C_5H_5)(R_2R'P)(R'')Ni$ complexes described in this paper have been recorded in carbon disulfide solution, and the data are summarized in Table I. The spectrum of each product is consistent with the structure assigned. It is of additional interest to note that the replacement of a chlorine substituent in **1** by a highly electronegative σ-bonded organic substituent results in an appreciable shift of the corresponding π-cyclopentadienyl proton resonance to lower field. On the other hand, the π-cyclopentadienyl resonance of the methyl derivative **10** fell at essentially the same chemical shift as the corresponding resonance in **1**, whereas in the case of the phenyl derivative **9**, this resonance was only slightly shifted to lower field. In contrast, replacement of a chlorine substituent in the diphenylmethylphosphine complex **2** by either a pentafluorophenyl or a pentachlorophenyl substituent resulted in appreciable *shielding* of the corresponding methyl protons on phosphorus. Analogous trends were also observed in deuteriochloroform solution; however, the methyl derivative **10** proved to be so reactive in this solvent that its proton nmr spectra could not satisfactorily be measured.

The above trends in the π-cyclopentadienyl resonances as a function of the σ-bonded substituent on nickel contrast sharply to similar trends involving the replacement of chlorine substituents in titanocene dichloride with methyl, phenyl, or perhaloaryl substituents.[22,23] In each of these cases, the π-cyclopentadienyl resonance is invariably shifted to substantially *higher* field on introduction of the σ-bonded organic substituent. Differing geometries between the nickel and titanium systems may well account for these diverse trends. We hope that additional spectral and structural studies on these and related series of σ-bonded organic transition metal compounds will be useful in a better understanding of such trends.

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[20] G. Booth and J. Chatt, *Proc. Chem. Soc.*, 67 (1961); *J. Chem. Soc., A*, 634 (1966).

[21] E. A. Hartman and A. Wojcicki, *Inorg. Chem.*, **7**, 1504 (1968), and references cited therein.

[22] H. C. Beachell and S. A. Butter, *ibid.*, **4**, 1133 (1965).

[23] H. B. Gordon and M. D. Rausch, unpublished studies.

TABLE I

PROTON NMR SPECTRA OF SOME ORGANONICKEL COMPOUNDS IN CARBON DISULFIDE SOLUTION

		Chemical shift and multiplicity[a]			
No.	Compound	π-C_5H_5	σ-R	CH_3P	C_6H_5P
4	$[(C_6H_5)_3P]_2(C_6F_5)_2Ni$				2.67 m
6	$[(C_6H_5)_2CH_3P]_2(C_6F_5)_2Ni$			8.38 t[b]	2.68 m
1	(π-C_5H_5)$[(C_6H_5)_3P]NiCl$	5.09 s			2.43 m
2	(π-C_5H_5)$[(C_6H_5)_2CH_3P]NiCl$	5.08 s		8.06 d[c]	2.44 m
3	(π-C_5H_5)$[(C_6H_5)_3P](C_6F_5)Ni$	4.83 s			2.56 m
5	(π-C_5H_5)$[(C_6H_5)_2CH_3P](C_6F_5)Ni$	4.90 s		8.45 d[c]	2.52 m
7	(π-C_5H_5)$[(C_6H_5)_3P](C_6Cl_5)Ni$	4.80 s			2.65 m
8	(π-C_5H_5)$[(C_6H_5)_2CH_3P](C_6Cl_5)Ni$	4.84 s		8.42 d[c]	2.57 m
9	(π-C_5H_5)$[(C_6H_5)_3P](C_6H_5)Ni$	4.97 s	3.60 m		2.80 m
10	(π-C_5H_5)$[(C_6H_5)_3P](CH_3)Ni$	5.09 s	11.00 d[d]		2.62 m
11	(π-C_5H_5)$[(C_6H_5)_3P](CF_3)Ni$	4.85 s			2.52 m
12	(π-C_5H_5)$[(C_6H_5)_3P](n\text{-}C_3F_7)Ni$	4.87 s			2.52 m
13	(π-C_5H_5)$[(n\text{-}C_4H_9)_3P](CH_3)Ni$[e]	5.12 s	11.16 d[d]		
14	(π-C_5H_5)$[(C_6H_5)_3P](SO_2CH_3)Ni$	4.77 s	7.57 s		2.50 m
15	(π-C_5H_5)$[(n\text{-}C_4H_9)_3P](SO_2CH_3)Ni$[f]	4.67 s	7.17 s		

[a] Given in τ units (ppm) (estimated accuracy ±0.02 ppm). Abbreviations: s, singlet; d, doublet; m, multiplet. [b] $J = 4$ Hz. [c] $J = 10$ Hz. [d] $J = 6$ Hz. [e] Resonances due to the *n*-butyl substituent were observed at τ 8.62 m and τ 9.03 m. [f] Resonances due to the *n*-butyl substituent were observed at τ 8.40 m and τ 9.03 m.

Experimental Section

Infrared spectra were recorded on a Beckman IR-10 spectrophotometer. Proton nmr spectra were recorded on a Varian A-60 spectrometer with tetramethylsilane as an internal standard. Melting points were determined under nitrogen unless otherwise mentioned on a Mel-Temp apparatus and are uncorrected. Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and by Mr. Charles Meade of the University of Massachusetts Microanalytical Laboratory. Ethyl ether was purified by distillation from sodium wire or calcium hydride. Tetrahydrofuran was purified by distillation from lithium aluminum hydride. Water was removed from benzene by azeotropic distillation. Hexane was purified by treatment with concentrated sulfuric acid, subsequent drying over calcium chloride, and distillation; the distilled solvent was stored over sodium wire. Nickelocene was obtained from the Arapahoe Chemical Co. and was freshly sublimed before use. *n*-Butyllithium (in hexane solution) was purchased from Alfa Inorganics, Inc., and bromopentafluorobenzene was from the Imperial Smelting Corp., Ltd. Hexachlorobenzene (Eastman Organic Chemicals Co.) was purified by recrystallization from benzene and subsequently from hexane to yield white needles, mp 228–229°.

π-Cyclopentadienyl(diphenylmethylphosphine)nickel Chloride (2).—A modification of the procedure of Schroll[8] was employed. Bis(diphenylmethylphosphine)dichloronickel[24] was prepared in 91% yield as bright maroon crystals which started to decompose at 146° (lit.[24] mp 148–150°). The nmr spectrum in deuteriochloroform solution exhibited resonances at τ 5.23 (phenyl protons) and τ 7.11 (methyl protons); the latter appeared as a triplet due to spin–spin interaction with the two magnetically equivalent phosphorus nuclei.

In a nitrogen atmosphere, 2.5 g (5 mmol) of bis(diphenylmethylphosphine)dichloronickel and 100 ml of tetrahydrofuran were added to a 250-ml three-necked flask. With rapid stirring, 0.95 g (5 mmol) of nickelocene dissolved in 50 ml of tetrahydrofuran was added to the solution over a period of 20 min. After the addition was complete, the reaction mixture was heated to reflux for 8 hr and then allowed to cool to room temperature. The solvent was removed under reduced pressure. Hot benzene was added to dissolve the residue and the resultant mixture was filtered and concentrated to *ca.* 15 ml. An excess of hexane was added, causing the precipitation of 2.6 g (73% yield) of 2 as a maroon solid. Recrystallization from hexane–benzene (5:1) gave a product which decomposed at 112–114°. *Anal.* Calcd for $C_{18}H_{18}ClNiP$: C, 60.14; H, 5.05; Ni, 16.33. Found: C, 59.75; H, 5.17; Ni, 16.38. An infrared spectrum (KBr pellet) exhibited aromatic C–H absorption at 3060 cm^{-1} and aliphatic C–H absorption at 2910 cm^{-1}.

π-Cyclopentadienyl(triphenylphosphine)nickel Chloride (1).—In an analogous manner, bis(triphenylphosphine)dichloronickel (13.1 g, 0.02 mol) and nickelocene (3.8 g, 0.02 mol) produced 1 in 84% yield. Recrystallization from hexane–benzene (5:1) gave maroon crystals which decomposed in air at 141° (lit.[8] mp 140°). When taken under nitrogen, the melting point was 166–168°.

Reaction of π-Cyclopentadienyl(triphenylphosphine)nickel Chloride (1) and Pentafluorophenyllithium.—Bromopentafluorobenzene (2.47 g, 10 mmol) and 50 ml of ethyl ether were added to a 500-ml three-necked flask which was equipped with a nitrogen inlet, condenser, addition funnel, and a magnetic stirring bar and which had previously been purged three times with dry, prepurified nitrogen. The flask and its contents were cooled to −78° and 10 mmol of *n*-butyllithium in hexane together with 50 ml of ethyl ether were added with rapid stirring over a period of 30 min. π-Cyclopentadienyl(triphenylphosphine)nickel chloride (4.22 g, 10 mmol) in 200 ml of ethyl ether was subsequently added with stirring to the pentafluorophenyllithium solution over a period of 30 min at −78°. After the addition was complete, the reaction mixture was allowed to warm to room temperature with stirring. Following hydrolysis with 50 ml of saturated ammonium chloride solution, the organic layer was washed twice with water and was dried over anhydrous magnesium sulfate. The solvent was removed and the dark green residue was dissolved in benzene and chromatographed on neutral alumina. A dark green band was eluted with a hexane–benzene (1:1) mixture. After removal of the solvent, the residue was recrystallized from hexane to give dark green needles with a small amount of yellow crystals. Since the former were more soluble in hexane than the latter, the two compounds were separated by several successive recrystallizations.

The dark green needles, purified by recrystallization from hexane, amounted to 4.5 g (81% yield) of π-cyclopentadienyl-σ-pentafluorophenyl(triphenylphosphine)nickel (**3**), mp 214–215° dec. *Anal.* Calcd for $C_{29}H_{20}F_5NiP$: C, 62.97; H, 3.64; Ni, 10.62. Found: C, 62.86; H, 3.53; Ni, 10.63. The infrared spectrum of **3** (KBr pellet) showed characteristic absorptions[5] of the pentafluorophenyl group at 945, 1040, and 1050 cm^{-1}.

Recrystallization of the yellow solid from a benzene–methanol (1:2) mixture gave 0.19 g of material which melted with decomposition at 202–205°. An nmr spectrum of the yellow solid in carbon disulfide exhibited a single multiplet centered at τ 2.67. In the infrared spectrum (KBr pellet), strong bands attributable to a pentafluorophenyl group were observed at 959, 1040, and

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[24] R. G. Hayter and F. S. Humiec, *Inorg. Chem.*, **4**, 1701 (1965).

1050 cm^{-1}. A comparison of the infrared spectra and a mixture melting point determination showed this compound to be identical with an authentic sample of bis(triphenylphosphine)bis(σ-pentafluorophenyl)nickel (**4**).[5] The yield of **4** was approximately 4%.

Reaction of π-Cyclopentadienyl(diphenylmethylphosphine)nickel Chloride (2) and Pentafluorophenyllithium.—The reaction was analogous to that described above for **1** and pentafluorophenyllithium, employing 5 mmol of the latter reagent and 1.38 g (4 mmol) of **2**. After chromatography there remained dark green crystals contaminated by a small amount of yellow crystals. The former were purified by recrystallization from hexane to give 1.3 g (74% yield) of π-cyclopentadienyl-σ-pentafluorophenyl-(diphenylmethylphosphine)nickel (**5**), mp 104–105° dec. *Anal.* Calcd for $C_{24}H_{18}F_5NiP$: C, 58.70; H, 3.70; F, 19.34; Ni, 11.96. Found: C, 58.41; H, 3.87; F, 19.22; Ni, 12.30. The infrared spectrum of **5** (KBr pellet) exhibited characteristic absorptions[5] of the pentafluoro group at 947, 1045, and 1055 cm^{-1}.

The yellow crystals were recrystallized several times from hexane to give 70 mg (*ca.* 4%) of product, mp 193.5–194° dec. *Anal.* Calcd for $C_{38}H_{26}F_{10}NiP$: C, 57.54; H, 3.30; F, 23.95; Ni, 7.40; P, 7.81. Found: C, 57.35; H, 3.15; F, 23.84; Ni, 7.10; P, 8.08. Characteristic absorptions[5] of a pentafluorophenyl group were noted at 945, 1040, and 1050 cm^{-1} in the infrared spectrum (KBr pellet) of the product. On the basis of elemental analysis and infrared and nmr data and by a comparison with a sample prepared from the reaction of bis(diphenylmethylphosphine)dichloronickel and pentafluorophenyllithium,[13] the yellow crystals were identified as bis(diphenylmethylphosphine)-bis(σ-pentafluorophenyl)nickel (**6**).

π-Cyclopentadienyl-σ-pentachlorophenyl(triphenylphosphine)nickel (7).—In an analogous manner, a reaction between pentachlorophenyllithium [prepared from 2.85 g (10 mmol) of hexachlorobenzene and 10 mmol of *n*-butylithium in hexane at −78°][14] and 4.22 g (10 mmol) of **1** produced, after chromatography on alumina, 3.65 g (61% yield) of dark green crystals of **7**. The latter melted with decomposition at 201.5–202.5°. *Anal.* Calcd for $C_{29}H_{20}Cl_5NiP$: C, 54.81; H, 3.17; Cl, 27.89; Ni, 9.24; P, 4.87. Found: C, 54.73; H, 3.25; Cl, 27.50; Ni, 9.13; P, 4.68. The infrared spectrum (KBr pellet) exhibited absorptions at 665 and 835 cm^{-1} which are characteristic[14] of the pentachlorophenyl group.

π-Cyclopentadienyl-σ-pentachlorophenyl(diphenylmethylphosphine)nickel (8).—The reaction was analogous to that described for **1** and pentachlorophenyllithium, employing 5 mmol of the latter reagent and 1.43 g (5 mmol) of **2**. After chromatography on alumina and subsequent recrystallization from hexane, 0.91 g (53% yield) of **10** was isolated in the form of dark green crystals. The product melted with decomposition at 152–154°. *Anal.* Calcd for $C_{24}H_{18}Cl_5NiP$: C, 50.27; H, 3.17; Cl, 30.91; Ni, 10.25; P, 5.40. Found: C, 50.02; H, 3.59; Cl, 30.55; Ni, 10.54; P, 5.20. An infrared spectrum (KBr pellet) exhibited absorptions at 667 and 837 cm^{-1} which are characteristic[14] of the pentachlorophenyl group.

π-Cyclopentadienyl-σ-phenyl(triphenylphosphine)nickel (9).—A reaction between 1.3 g (3 mmol) of **1** dissolved in 100 ml of 1:1 ethyl ether–benzene and 3 mmol of phenyllithium in ethyl ether–benzene solution (Alfa Inorganics) at −10° produced, after chromatography on alumina, 0.67 g (48% yield) of dark green crystals of **9**. The latter, after recrystallization from hexane, melted with decomposition at 134–135° (lit.[6] mp 137–139°). *Anal.* Calcd for $C_{29}H_{25}NiP$: C, 75.20; H, 5.44; Ni, 12.67; P, 6.69. Found: C, 75.58; H, 5.41; Ni, 12.00; P, 6.77.

π-Cyclopentadienyl-σ-methyl(triphenylphosphine)nickel (10).—A solution of 2.6 g (6 mmol) of **1** and 80 ml of benzene was cooled to 0°. With rapid stirring, 6 mmol of methyllithium in ethyl ether (Alfa Inorganics) was added dropwise, and the reaction mixture was subsequently allowed to warm to room temperature and was hydrolyzed with deoxygenated aqueous ammonium chloride. The organic layer was separated, washed with water, and dried, and the solvent was removed. The residue was recrystallized under nitrogen from hexane to give 1.0 g (40% yield) of **10** which melted with decomposition starting at 123° (lit.[6] mp 126–129°). *Anal.* Calcd for $C_{24}H_{23}NiP$: C, 71.86; H, 5.78; P, 7.72. Found: C, 71.87; H, 5.80; P, 7.76. The infrared spectrum of **10** (KBr pellet) exhibited C–H stretching modes of the π-cyclopentadienyl and σ-methyl groups at 3060 and 2950 cm^{-1}, respectively.

Alternatively, a reaction between **1** in ethyl ether and methylmagnesium chloride in tetrahydrofuran (Fisher Scientific Co.) followed by hydrolysis and chromatography on Florisil with pentane as eluent afforded **10**, mp 126–128° (N_2), in 55% yield.

π-Cyclopentadienyl-σ-trifluoromethyl(triphenylphosphine)nickel (11).—An improved, simplified modification of the original method described by Stone, *et al.*,[15] was employed. Bis(π-cyclopentadienyl)dicarbonyldinickel (2.42 g, 7.96 mmol), 30 ml of ethyl ether, and a magnetic stirring bar were placed into a 240-ml pressure bottle, and the system was flushed with nitrogen. Iodotrifluoromethane (5.10 g, 2.0 ml, 26 mmol), previously condensed, was then distilled into the pressure bottle which was cooled to −78°. The bottle was tightly capped, and the bottle and its contents were allowed to warm to room temperature over a period of 1.25 hr, during which time the reaction mixture was stirred magnetically. After this period, the bottle was again cooled to −78° and opened, and a protective blanket of nitrogen was maintained over the mixture. The solvent was removed *via* a water aspirator without the application of heat. The residue was placed in a high vacuum system and distilled at room temperature from trap to trap. The temperature of the first trap was −15°; the second and third traps were maintained at 0°. From this distillation, 430 mg (25% yield) of a red-purple liquid, π-cyclopentadienyl-σ-trifluoromethyl(carbonyl)nickel, was obtained.

The latter product (430 mg, 1.95 mmol) was combined with triphenylphosphine (513 mg, 2.15 mmol) and 30 ml of dichloromethane. The reaction mixture was stirred at room temperature for 3 hr, the solvent was removed *via* a water aspirator, and the green residue was recrystallized from ethyl ether–pentane to give 660 mg (75% yield) of **11** as green crystals, mp 160–161°. *Anal.* Calcd for $C_{24}H_{20}F_3NiP$: C, 63.34; H, 4.40; P, 6.79. Found: C, 63.30; H, 4.29; P, 6.80.

π-Cyclopentadienyl-σ-heptafluoropropyl(triphenylphosphine)nickel (12).—In an analogous manner, π-cyclopentadienyl-σ-heptafluoropropyl(carbonyl)nickel was prepared in 25% yield. A subsequent reaction of 369 mg (1.15 mmol) of this product with 305 mg (1.17 mmol) of triphenylphosphine in 30 ml of dichloromethane as described above resulted in 529 mg (83% yield) of green crystals of **12**, mp 145.5–147°. An analytical sample, mp 147–148°, was prepared by recrystallization of the product from pentane. *Anal.* Calcd for $C_{26}H_{20}F_7NiP$: C, 56.26; H, 3.63; P, 5.58. Found: C, 56.30; H, 3.54; P, 5.84.

Reaction of Sulfur Dioxide with π-Cyclopentadienyl-σ-methyl(triphenylphosphine)nickel.—π-Cyclopentadienyl-σ-methyl(triphenylphosphine)nickel (220 mg, 0.55 mmol) was placed in a test tube with a side arm. Sulfur dioxide was flushed through the tube for 3 min, and the tube was then cooled to −78°. Condensation of sulfur dioxide was continued until all of the starting material had dissolved to form a brown solution (*ca.* 10 ml required). The reaction mixture was maintained at −78° for 1 hr and was subsequently allowed to warm to room temperature, during which time the excess sulfur dioxide evaporated. The residue was extracted with warm dichloromethane, and the extracts were filtered and treated with hexane at reflux to produce 114 mg (45% yield) of dark green crystals of π-cyclopentadienyl-S-methylsulfinato(triphenylphosphine)nickel (**14**). The product did not melt, but underwent a color change at *ca.* 130°, followed by decomposition at *ca.* 195°. An analytical sample was prepared by recrystallization of the product from dichloromethane-hexane. *Anal.* Calcd for $C_{24}H_{23}NiO_2PS$: C, 61.96; H, 4.98; Ni, 12.62; S, 6.89. Found: C, 61.95; H, 4.97; Ni, 12.91; S, 6.89.

π-Cyclopentadienyl-S-methylsulfinato(tri-*n*-butylphosphine)nickel (15).—By a procedure similar to that described above, 348 mg (1.05 mmol) of π-cyclopentadienyl-σ-methyl(tri-*n*-butylphosphine)nickel (**13**)[6] and *ca.* 15 ml of liquid sulfur dioxide afforded 143 mg (30% yield) of **15** as green crystals, mp 77.5–78°. *Anal.* Calcd for $C_{27}H_{29}NiO_2PS$: C, 53.35; H, 8.71; P, 7.65; S, 7.81. Found: C, 53.20; H, 8.67; P, 7.68; S, 7.90.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Bidentate Bis(N-substituted 2-acetiminodimedonato)nickel(II) Complexes

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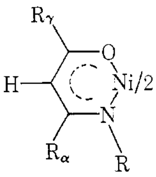
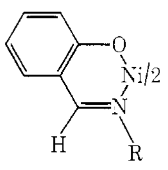
Bis(N-substituted 2-acetiminodimedonato)nickel(II) complexes, where the substituent (R) is H, CH_3, *i*-C_3H_7, *sec*-C_4H_9, C_6H_5, *o*-$C_6H_4CH_3$, *p*-$C_6H_4CH_3$, or $C_6H_5CHCH_3$, have been synthesized and their magnetic and spectral properties investigated. All of the complexes are predominantly planar in the solid phase, and all but the three α-branched alkyl derivatives are planar in chloroform solution. The α-branched alkyl complexes exhibit a planar–tetrahedral equilibrium in solution with the amount of tetrahedral form less than 10% at room temperature and increasing in the order $C_6H_5CHCH_3 <$ *sec*-$C_4H_9 <$ *i*-C_3H_7. Analysis of the temperature dependence of the proton contact shifts has yielded $\Delta G°$, $\Delta H°$, and $\Delta S°$ for the configurational interconversion. In comparison to analogous β-ketoamine– and salicylaldimine–nickel(II) complexes, dimedone promotes a planar configuration and hinders molecular association.

Introduction

Nickel(II) complexes of bidentate N-substituted β-ketoamines (A) and salicylaldimines (B) have been widely investigated.[2–5] Two types of equilibria have been reported: (1) between planar monomeric species and associated, quasioctahedral forms, the association being either solute–solute or solute–solvent, and (2) between planar and tetrahedral configurations. In general the salicylaldimines favor the associated and planar forms more than the β-ketoamine derivatives do.



A



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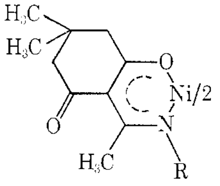

C

Bis(N-substituted 2-acetiminodimedonato)nickel(II) complexes (C) (dimedone = 5,5-dimethyl-1,3-cyclohexanedione) offer an important extension to the study, because the ligand has a conjugated chelate ring comparable to that of A and B and yet it contains a nonaromatic ring instead of the straight chain of A or the aromatic ring of B. Such perturbations of the ligand "backbone" may affect significantly the stereochemistry of the nickel complexes. In a preliminary investigation, we found that the dimedone system appears to promote a nonassociated, planar configuration about the nickel ion.[6]

The selection of nitrogen substituents in our study of complexes of type C includes R = CH_3, α-branched *sec*-alkyl groups, and aryl moieties,[7] since it has been reported[2,3,8] that in A and B complexes branching of an alkyl group at the carbon adjacent to nitrogen enhances the per cent of tetrahderal form while the R = aryl complexes exhibit some molecular associations. The order of association is *o*-$C_6H_4CH_3 >$ *p*-$C_6H_4CH_3$ for the A compounds and *o*-$C_6H_4CH_3 <$ *p*-$C_6H_4CH_3$ for the B compounds. Because the planar–tetrahedral equilibrium displayed by complexes A and B is affected by the configuration at asymmetric ligand centers,[2,9] two ligands chosen for this study have optically active centers.

Experimental Section

Preparation of Ligands.—2-Acetyldimedone was synthesized by the procedure of Smith.[10] The N-substituted 2-acetiminodimedone ligands were prepared by treating the appropriate primary amine with 2-acetiminodimedone according to the method of Dudek and Volpp.[11] The products were purified by crystallization and were identified by their proton resonance spectra;[12] they were not further characterized.

Preparation of Complexes.—Complexes were prepared by a

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