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Multinuclear NMR spectroscopic studies of some organometallic N-substituted anilines

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Abstract

Proton, carbon-13, nitrogen-15, fluorine-19, and silicon-29 NMR chemical shifts and coupling constants are reported for nine *N*-substituted anilines of the type $XC_6H_4N(H)Y$, where X = H and F, and $Y = Si(CH_3)_3$, $Ge(CH_3)_3$, $Sn(CH_3)_3$, and $P(BH_3)(CH_3)_2$, and the ^{15}N isotopomer of *N*-trimethylsilylaniline. Resonances in the natural-abundance carbon-13 NMR spectra for both sets of derivatives are assigned on the basis of additivity relationships, proton-coupled spectra, and relative magnitudes of $|J(^{31}P-^{13}C)|$ and $|J(^{19}F-^{13}C)|$ coupling constants where appropriate. Carbon-13 and fluorine-19 chemical shifts, and $|^1J(^{13}C-^1H)|$ coupling constants indicate that the $P(BH_3)(CH_3)_2$ group is substantially electron-withdrawing.

Introduction

The understanding of steric hindrance and electronic effects in organometallic compounds can be improved through the study of substituted aryl derivatives when careful comparisons are made with model analogs. Previous studies of homologous aryl derivatives containing main group element attachments to the aromatic ring have concentrated on *ortho*-, *meta*-, and *para*-substituted derivatives of groups 13–15, with aryltrimethylsilanes and -stannanes receiving the most scrutiny.

Our current investigations stem from our interest in the application of NMR spectroscopy to the analysis of substituent effects in aryltrimethylsilanes and

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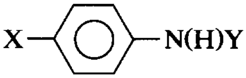
-germanes [1,2], -stannanes [2–8], aryldimethylphosphines and -arsines [1], and in traditional aromatic systems, including toluenes, anisoles, t-butylbenzenes, trifluorotoluenes, and *N*,*N*-dimethylanilines [2,9–11], and benzaldehydes [10–12]. The availability of NMR data for a variety of substituted aryldimethylphosphaneboranes [13–16] affords the opportunity to assess the substituent effects of the $P(BH_3)(CH_3)_2$ group. These effects can then be compared with those of the isoelectronic group $Si(CH_3)_3$.



X = H and F; Y = $Si(CH_3)_3$, $Ge(CH_3)_3$, $Sn(CH_3)_3$, and $P(BH_3)(CH_3)_2$

Experimental

Compounds

All procedures were carried out under an argon or nitrogen atmosphere using oven-dried glassware and dry reagents. Commercial n-butyllithium was purchased (Aldrich Chemical Company) as a 2.5 *M* solution in hexanes. Nitrogen-15 enriched aniline (95%) was purchased from Merck and was used without further purification in a microsynthetic synthesis of labeled *N*-trimethylsilylaniline. Solvents were normally removed under vacuum using a Büchi/Brinkmann Rotavapor-R rotary evaporation system or under high vacuum using a trapped oil pump. Vacuum distillations were performed on a 12-inch jacketed column packed with glass beads or helices and surmounted with an Ace Mini-Lab® distillation head. Melting points were obtained on a Thomas–Hoover capillary melting point apparatus and are uncorrected. Purity of all compounds probably exceeded 95%, as indicated by the absence of spurious signals in all NMR spectra. Carbon and hydrogen combustion analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

N-Substituted anilines were prepared in 60–80% yields according to one of the following two methods: (1) reaction of equimolar amounts of the chloro substituent with the appropriate aniline in the presence of a slight excess of triethylamine (T), followed by gravity filtration of the resulting triethylamine hydrochloride salt through Celite and vacuum distillation; or (2) reaction of the chloro substituent with the appropriate N-lithioaniline (L) (from equimolar amounts of n-butyllithium and the appropriate aniline), followed by filtration of lithium chloride through Celite and vacuum distillation. Solvents were removed under vacuum, and final products were isolated by vacuum distillation or by recrystallization from ether/pentane. Methods of preparation and boiling points for the $XC_6H_4N(H)Y$ derivatives are as follows: H, $Si(CH_3)_3$ (L), b.p. 28–31°C/0.08–0.10 Torr (lit. [17] b.p. 98–99°C/19 Torr); H, $Si(CH_3)_3$ ^{15}N isotopomer (L), b.p. 29–31°C/0.09–0.10 Torr (lit. [18] b.p. 106–107°C/24 Torr); F, $Si(CH_3)_3$ (T), b.p. 105–106°C/15–16 Torr (lit. [19] b.p. 106–107°C/21 Torr); H, $Ge(CH_3)_3$ (L), b.p. 100–102°C/7–8 Torr (lit. [18] b.p. 85–86°C/4 Torr and 67–68°C/1 Torr); H, $Sn(CH_3)_3$ (L), b.p. 71–72°C/0.025 Torr (lit. [18,20] b.p. 77°C/0.05 Torr).

p-*Fluoro*-N-*(trimethylgermyl)aniline.* Prepared in 70% yield from the reaction of *p*-fluoroaniline (8.8 g, 0.079 mol), trimethylgermanium chloride (12.1 g, 0.079 mol), and triethylamine (8.0 g, 0.079 mol) in benzene as described. The product distilled as a colorless liquid (b.p. 98–100°C/4.5–5.0 Torr). ^1H NMR (C_6D_6, 60 MHz): δ 6.4–7.3 (m, 4 H, C_6H_4); 3.0–3.5 (br, 1 H, NH); 0.6 (s, 9 H, $GeMe_3$). Anal. Found: C, 48.31; H, 5.99. $C_9H_{14}FGeN$ calc.: C, 47.45; H, 6.19%.

p-*Fluoro*-N-*(trimethylstannyl)aniline.* Obtained in 50% yield from the reaction of *p*-fluoroaniline (17.8 g, 0.16 mol), trimethyltin chloride (39.9 g, 0.20 mol), and triethylamine (20.2 g, 0.20 mol) in benzene as described. The product was recrystallized from ether/pentane (50:50) as colorless crystals (m.p. 68–69°C). ^1H NMR (C_6D_6, 60 MHz): δ 6.4–7.4 (m, 4 H, C_6H_4); 3.0–3.5 (br, 1 H, NH); 0.8 (s, 9 H, $SnMe_3$). Anal. Found: C, 39.82; H, 5.21. $C_9H_{14}FNSn$ calc.: C, 39.47; H, 5.15%.

N-*(Dimethylphosphaneborane)aniline.* Secured in 30% yield according to the method of Schmidbaur [15], in 50% yield from the reaction of aniline (8.7 g, 0.093 mol) in 30 mL of ether with 30 mL of a THF solution of dimethylchlorphosphaneborane [15,21,22] (5.2 g, 0.047 mol) (Strem Chemicals Inc.). A white precipitate formed immediately, and this was removed by suction filtration in a glove bag. The resulting pale yellow filtrate was evaporated to dryness under vacuum. The remaining sticky white solid was washed three times with n-pentane, and it then was dried on a vacuum line to yield a white solid (m.p. 59–60°; lit. [15] m.p. 57°C). Proton NMR parameters are consistent with those reported [15].

p-*Fluoro*-N-*(dimethylphosphaneborane)aniline.* Prepared in 30% yield from the dropwise addition of freshly distilled *p*-fluoroaniline (4.1 g, 0.037 mol) and triethylamine (3.8 g, 0.037 mol) in 60 mL of ether to a solution of dimethylchlorphosphaneborane (3.6 g, 0.033 mol) in 30 mL of ether contained in a 250 mL three-necked roundbottom flask fitted with a magnetic stir bar. Immediately upon addition of the amine solution, a white precipitate formed and the flask became warm to the touch. After 3 h, the contents were transferred to centrifuge tubes, and the white precipitate was compacted by centrifugation. The organic layers were separated and combined in a glove bag, and the solvent was evaporated under vacuum. The resulting yellow sludge was recrystallized three times from a 50:50 mixture of ether/pentane to yield a waxy yellow solid (m.p. 63–65°C). ^1H NMR (C_6D_6, 60 MHz): δ 7.4–6.4 (m, 4 H, C_6H_4); 3.89 (d, 1 H, NH); 0.30 (s, 6 H, PMe_2); 0.60 (dq, 3 H, BH_3). Anal. Found: C, 50.85; H, 7.37. $C_8H_{14}BFNP$ calc.: C, 51.94; H, 7.63%.

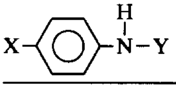
NMR parameters

Proton spectra were recorded in the continuous wave mode on a Varian EM-360A spectrometer operating at 60 MHz. All other spectra were obtained in the Fourier transform mode on JEOL FX 90-Q and Varian VXR-400 spectrometers. Spectra were recorded on the JEOL FX 90-Q using the following acquisition parameters: observation frequency, acquisition time, pulse width, frequency width, pulse delay, and number of data points. For ^{13}C: 22.49 MHz, 1.6 s, 8 μs, 5000 Hz, 10 s, 16K; for ^{19}F: 84.25 MHz, 0.4 s, 10 μs, 5000 Hz, 5 s, 16 K; and for ^{29}Si: 17.75 MHz, 1.6 s, 13 μs, 5000 Hz, 10 s, 16K. Spectra recorded on the Varian VXR-400 employed the following acquisition parameters: observation frequency, acquisition time, pulse width, frequency width, pulse delay, and number of data points. For ^{13}C: 101 MHz, 1 s, 5 μs, 25000 Hz, 0 s, 40K; for ^{15}N: 41.0 MHz, 1.1 s, 10 μs, 20000 Hz, 5 s, 43K; and for ^{29}Si: 79.0 MHz, 1 s, 15.0 μs, 25000 Hz, 10 s, 40K.

Samples were contained in tubes with outer diameter 10 mm. Spectra were normally recorded as 50% (w/v or v/v) solutions in C_6D_6. Chemical shifts

Table 1

Proton, nitrogen-15, fluorine-19 and silicon-29 NMR data for *N*-substituted anilines



X	Y	$\delta(^1H)Y$ [a]	$\delta(^1H{-}N)$ [a]	$\delta(^{15}N)$ [b]	$\delta(^{19}F)$ [c]	$\delta(^{29}Si)$ [d]
H	$Si(CH_3)_3$	0.07	2.92	45.04	–	2.31
H	$Si(CH_3)_3$ [e]	0.11	3.05 [f]	44.97 [g]	–	1.83
F	$Si(CH_3)_3$	0.15	3.20	–	−124.96	2.91
H	$Ge(CH_3)_3$	0.30	2.90	34.69	–	–
F	$Ge(CH_3)_3$	0.31	2.72	31.20	−126.97	–
H	$Sn(CH_3)_3$	0.18 [h]	2.77	35.32	–	–
F	$Sn(CH_3)_3$	0.30 [i]	2.65	31.42	−126.60	–
H	$P(BH_3)(CH_3)_2$	1.40 [j]	5.03 [k]	40.90 [l]	–	–
F	$P(BH_3)(CH_3)_2$	1.08 [m]	4.35 [n]	36.95 [o]	−121.41	–

[a] Relative to TMS in ppm. [b] Relative to NH_4^+ in ppm. [c] Relative to $CFCl_3$ in ppm. [d] Relative to TMS in ppm. [e] ^{15}N isotopomer. [f] $|^1J(^{15}N{-}^1H)| = 76.2$ Hz. [g] $|^1J(^{15}N{-}^{29}Si)| = 16.3$ Hz. [h] $|^2J(^{119,117}Sn{-}C{-}^1H)| = 57.6$, 55.2 Hz. [i] $|^2J(^{119,117}Sn{-}C{-}^1H)| = 58.6$, 56.0 Hz. [j] $|^2J(^{31}P{-}C{-}^1H)| = 10.0$ Hz. [k] $|^2J(^{31}P{-}N{-}^1H)| = 9.0$ Hz. [l] $|^1J(^{15}N{-}^{31}P)| = 20.3$ Hz. [m] $|^2J(^{31}P{-}C{-}^1H)| = 9.5$ Hz. [n] $|^2J(^{31}P{-}N{-}^1H)|$ = broad. [o] $|^1J(^{15}N{-}^{31}P)| = 21.2$ Hz.

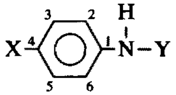
obtained in this way are believed to be accurate and reproducible to within ±0.05 ppm, while coupling constants are reliable to ±0.2 Hz. Data point resolution based on these sampling conditions indicates a maximum error of approximately ±0.6 Hz in values obtained from ^{13}C and ^{29}Si spectra; multiple spectra of the same compound afforded a reproducibility approaching ±0.4 Hz for chemical shifts and coupling constants (determined using standard deviation). Chemical shift reference compounds were internal tetramethylsilane (TMS) for ^1H, ^{13}C and ^{29}Si; external hexafluorobenzene, and reported relative to $CFCl_3$, for ^{19}F; and external aqueous ammonium nitrate (the NH_4^+ nitrogen atom) for ^{15}N. For N-trimethylsilylanilines, ^{13}C and ^{29}Si spectra were recorded both in the absence and presence of TMS to confirm the identity of the appropriate trimethylsilyl nuclei. External reference materials were contained in coaxial inner cells. Ambient probe temperature was 25°C in the JEOL and 23°C in the Varian.

Results

Table 1 presents proton, nitrogen-15, fluorine-19, and silicon-29 NMR chemical shifts for nine derivatives. Table 2 contains carbon-13 chemical shifts for these compounds. Both Tables 1 and 2 also include appropriate coupling constants where available. NMR data for several derivatives are reported in previous literature, including *N*-trimethylsilylaniline [18,23–29], ^{15}*N*-trimethylsilylaniline [18,26], *p*-fluoro-*N*-trimethylsilylaniline [19], *N*-trimethylgermylaniline [18,23], *N*-trimethylstannylaniline [18,23,27,30,31], and *N*-(dimethylphosphaneborane)aniline [15]. Our values are in excellent agreement for determinations in similar solvents. Assignments of aromatic carbon resonances are based upon (1) additivity relationships among the ring carbon chemical shifts, (2) the number of directly attached protons, obtained from off-resonance and DEPT carbon-13 spectra, (3) relative magnitudes of $|J(^{19}F{-}^{13}C)|$ spin–spin coupling constants in the *para*-fluoro com-

Table 2

Carbon-13 NMR data for *N*-substituted anilines [a]



X	Y	δ C(1)	δ C(2,6)	δ C(3,5)	δ C(4)	δ Y
H	$Si(CH_3)_3$	147.66	116.56	129.53	117.94	0.01
H	$Si(CH_3)_3$ [b]	147.64	116.55	129.51	117.93	0.02
F	$Si(CH_3)_3$	144.64	117.80	116.44	156.68	0.55
F	$\|J(^{19}F-^{13}C)\|$ (Hz)	2.2	7.3	22.0	233.7	–
H	$Ge(CH_3)_3$	147.32	115.03	129.35	118.00	3.47
F	$Ge(CH_3)_3$	143.38	115.95	115.65	156.36	3.23
F	$\|J(^{19}F-^{13}C)\|$ (Hz)	1.8	7.4	22.3	234.0	–
H	$Sn(CH_3)_3$	147.21	115.00	129.39	118.18	−2.41 [c]
F	$Sn(CH_3)_3$	143.0	116.03	115.68	156.57	−1.28 [d]
F	$\|J(^{19}F-^{13}C)\|$ (Hz)	–	7.2	22.2	234.8	–
H	$P(BH_3)(CH_3)_2$	142.42	118.83 [f]	129.54	121.52	14.29 [g]
F	$P(BH_3)(CH_3)_2$	137.63	121.19	116.06	158.64	13.97
F	$\|J(^{19}F-^{13}C)\|$ (Hz)	2.6	7.6	22.6	240.4	–
F	$\|J(^{31}P-^{13}C)\|$ (Hz)	7.6	4.3	–	–	40.9

[a] Chemical shifts are in ppm relative to TMS. [b] ^{15}N isotopomer. $|^1J(^{15}N-^{13}C(1))| = 12.0$ Hz; $|^2J(^{15}N-^{13}C(2,6))| = 2.1$ Hz. [c] $|^1J(^{119}Sn-^{13}C)| = 395.8$ Hz; $|^1J(^{117}Sn-^{13}C)| = 378.4$ Hz. [d] $|^1J(^{119}Sn-^{13}C)| = 386.4$ Hz; $|^1J(^{117}Sn-^{13}C)| = 369.6$ Hz. [e] $|^2J(^{31}P-^{13}C(1))| = 6.0$ Hz. [f] $|^3J(^{31}P-^{13}C(2,6))| = 4.9$ Hz. [g] $|^1J(^{31}P-^{13}CH_3)| = 41.1$ Hz.

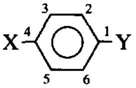
pounds and $|J(^{31}P-^{13}C)|$ values in the phosphorus–boron anilines, and (4) comparison of chemical shift data with similar information previously obtained for aromatic derivatives of Group 14 elements [1–6,8–14,32]. That the $P(BH_3)(CH_3)_2$ group remains intact during synthesis and workup is revealed by the characteristic broad "quartet of doublets" pattern observed in the proton NMR spectra of the phosphorus–boron compounds. In general, caution must be exercised in making distinctions between carbon atoms two and three bonds distant from phosphorus solely on the basis of coupling constants, owing to the similar magnitude of $|^2J(^{31}P-^{13}C)|$ and $|^3J(^{31}P-^{13}C)|$ in these systems [13,14]. It is well-known that $|^3J|$ is frequently greater than $|^2J|$ for coupling constants involving carbon-13 in aromatic systems. In contrast to early work on *ortho*- and polysubstituted aromatic systems in which additivity failed to predict shielding effects, there is good qualitative agreement (±1–3 ppm differences between calculated and observed shifts, at worst) when the carbon-13 chemical shifts of the *para*-fluoro derivatives are predicted by combining the shifts of the corresponding unsubstituted aniline and fluorobenzene [33] (Table 3).

Discussion

The preparation of the Group 14 and dimethylphosphaneborane aniline compounds proceeds smoothly, with higher yields for the former derivatives than for the latter. The previously observed [13,14] electron-withdrawing effect of the

Table 3

Additivity of carbon-13 chemical shifts for *N*-substituted anilines [a,b]



X	Y	δ C(1)	δ C(2, 6)	δ C(3, 5)	δ C(4)
F	H [c]	−4.5	+1.4	−12.9	+34.8
H	N(H)Si(CH$_3$)$_3$	+19.2	−11.9	+1.0	−10.6
F	N(H)Si(CH$_3$)$_3$ (calc.)	+14.7	−10.5	−11.9	+24.2
F	N(H)Si(CH$_3$)$_3$ (found)	+16.1	−10.7	−12.1	+28.2
F	H [c]	−4.5	+1.4	−12.9	+34.8
H	N(H)Ge(CH$_3$)$_3$	+18.8	−13.5	+0.9	−10.5
F	N(H)Ge(CH$_3$)$_3$ (calc.)	+14.3	−12.1	−12.0	+24.3
F	N(H)Ge(CH$_3$)$_3$ (found)	+14.9	−12.5	−12.9	+27.9
F	H [c]	−4.5	+1.4	−12.9	+34.8
H	N(H)Sn(CH$_3$)$_3$	+18.7	−13.5	+0.9	−10.3
F	N(H)Sn(CH$_3$)$_3$ (calc.)	+14.2	−12.1	−12.0	+24.5
F	N(H)Sn(CH$_3$)$_3$ (found)	+14.5	−12.5	−12.8	+28.1
F	H [c]	−4.5	+1.4	−12.9	+34.8
H	N(H)P(BH$_3$)(CH$_3$)$_2$	+13.9	−9.6	+1.1	−7.0
F	N(H)P(BH$_3$)(CH$_3$)$_2$ (calc.)	+9.4	−8.2	−11.8	+27.8
F	N(H)P(BH$_3$)(CH$_3$)$_2$ (found)	+9.1	−7.3	−12.4	+30.1

[a] Chemical shifts are expressed relative to internal benzene (128.5 ppm). [b] Shifts for unsubstituted anilines are from this study. [c] Ref. 33.

P(BH$_3$)(CH$_3$)$_2$ group does not appear to significantly affect the synthesis of the two aniline derivatives.

The data of Tables 1 and 2 show several interesting trends: (a) the NH proton shifts for the P(BH$_3$)(CH$_3$)$_2$ derivative are 2–3 ppm higher than the shifts of the other derivatives, which are approximately the same; (b) the ^{19}F shift for the P(BH$_3$)(CH$_3$)$_2$ derivative is higher than that of the Ge(CH$_3$)$_3$ and Sn(CH$_3$)$_3$ derivatives, while the shift for the Si(CH$_3$)$_3$ derivative is midway between; (c) the C(4) shift for the P(BH$_3$)(CH$_3$)$_2$ derivative is higher by more than 3 ppm than the corresponding shifts for the other derivatives, which are approximately the same (118.04 ± 0.14 ppm); (d) the one bond ^{13}C–^{19}F coupling constant at C(4) is higher by 6 Hz for the P(BH$_3$)(CH$_3$)$_2$ derivative than the constants for the other derivatives, which are 234.2 ± 0.6 Hz; (e) the ^{15}N chemical shifts vary Si(CH$_3$)$_3$ (45.0 ppm) $>$ P(BH$_3$)(CH$_3$)$_2$ (40.9 ppm) $>$ Sn(CH$_3$)$_3$ (35.3 ppm) $\geq$ Ge(CH$_3$)$_3$ (34.7 ppm).

All of these trends except the last can be explained by the previously observed [13,14] electron-withdrawing ability of the P(BH$_3$)(CH$_3$)$_2$ group, a result, presumably, of the electronegativity of the phosphorus, the formal positive charge on the phosphorus, and, possibly, $(p \rightarrow d)\pi$ interactions between the aromatic ring and phosphorus. The effect of electron-withdrawing groups on the chemical shifts and coupling constants is well documented [1–14,33]; in the case of ^{19}F and ^{13}C, the group removes electron density from the para position, thereby reducing r in the paramagnetic shift term and increasing the frequency of resonance.

The unexpectedly large ^{15}N shift for the $Si(CH_3)_3$ derivative can be attributed to a significant $(p \rightarrow d)\pi$ interaction between nitrogen and silicon, leading to a decrease in r at nitrogen and an increase in π-bonding. Both factors should produce, according to the paramagnetic term, a shift to higher frequencies. This rationalization suggests that the previous [13,14] hypothesis that the $P(BH_3)(CH_3)_2$ group withdraws electron density primarily by an electron-withdrawing inductive effect, rather than through a $(p \rightarrow d)\pi$ mechanism, has merit.

Acknowledgments

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References

1 R.E. Hess, C.K. Haas, B.A. Kaduk, C.D. Schaeffer, Jr. and C.H. Yoder, Inorg. Chim. Acta, 5 (1971) 161.
2 C.D. Schaeffer, Jr., J.J. Zuckerman and C.H. Yoder, J. Organomet. Chem., 80 (1974) 29.
3 C.D. Schaeffer, Jr. and J.J. Zuckerman, J. Organomet. Chem., 47 (1973) C1.
4 C.D. Schaeffer. Jr. and J.J. Zuckerman, J. Organomet. Chem., 55 (1973) 97; 59 (1973) C40.
5 C.D. Schaeffer, Jr. and J.J. Zuckerman, J. Organomet. Chem., 78 (1974) 373.
6 C.D. Schaeffer, Jr. and J.J. Zuckerman, J. Organomet. Chem., 99 (1975) 407.
7 M.E. Bishop, C.D. Schaeffer, Jr. and J.J. Zuckerman, Spectrochim. Acta, Part A, 32 (1976) 1519.
8 H.-J. Kroth, H. Schumann, H.G. Kuivila, C.D. Schaeffer, Jr., and J.J. Zuckerman, J. Am. Chem. Soc., 97 (1975) 1754.
9 C.H. Yoder, R.H. Tuck and R.E. Hess, J. Am. Chem. Soc., 91 (1969) 539.
10 R.E. Hess, C.D. Schaeffer, Jr. and C.H. Yoder, J. Org. Chem., 36 (1971) 2201.
11 C.H. Yoder, F.K. Sheffy, R. Howell, R.E. Hess, L. Pacala, C.D. Schaeffer, Jr. and J.J. Zuckerman, J. Org. Chem., 41 (1976) 1511.
12 C.H. Yoder, C.D. Schaeffer, Jr. and R.E. Hess, J. Chem. Eng. Data, 17 (1972) 385.
13 J.A. Albanese, D.G. Kreider, C.D. Schaeffer, Jr., C.H. Yoder and M.S. Samples, J. Org. Chem., 50 (1985) 2059; 50 (1985) 4666.
14 J.A. Albanese, D.E. Gingrich, C.D. Schaeffer, Jr., S.M. Coley, J.C. Otter, M.S. Samples and C.H. Yoder, J. Organomet. Chem., 365 (1989) 23.
15 H. Schmidbaur and E. Weiss, Angew. Chem., Int. Ed. Engl., 18 (1979) 781.
16 H. Schmidbaur, J. Organomet. Chem., 200 (1980) 287.
17 H.H. Anderson, J. Am. Chem. Soc., 73 (1951) 5802.
18 E.W. Randall and J.J. Zuckerman, J. Am. Chem. Soc., 90 (1968) 3167.
19 C.H. Yoder, Inorg. Nucl. Chem. Lett., 7 (1971) 637.
20 K. Jones and M.F. Lappert, J. Chem. Soc., (1965) 1944.
21 S.O. Grim and J.D. Mitchell, Phosphorus, 6 (1976) 89.
22 C.H. Yoder and L.A. Miller, J. Organomet. Chem., 228 (1982) 31.
23 E.W. Randall, J.J. Ellner and J.J. Zuckerman, J. Am. Chem. Soc., 88 (1966) 622.
24 H. Nöth, W. Tinhof and B. Wrackmeyer, Chem. Ber., 107 (1974) 518.
25 K. Barlos, G. Hübler, H. Nöth, P. Wanninger, N. Wiberg and B. Wrackmeyer, J. Magn. Reson., 31 (1978) 363.
26 E. Kupce, E. Liepins, O. Pudpva and E. Lukevics, J. Chem. Soc., Chem. Commun., (1984) 581.
27 B. Wrackmeyer, S. Kerschl, C. Stader and K. Horchler, Spectrochim. Acta, Part A, 42 (1986) 1113.
28 E. Kupce and E. Lukevics, J. Magn. Reson., 76 (1988) 63.

29 B. Wrackmeyer, C. Stader and H. Zhou, Spectrochim. Acta, Part A, 45 (1989) 1101.

30 J.D. Kennedy, W. McFarlane, G.S. Pyne and B. Wrackmeyer, J. Chem. Soc., Dalton Trans., (1975) 386.

31 J.D. Kennedy, W. McFarlane, G.S. Pyne and B. Wrackmeyer, J. Organomet. Chem., 195 (1980) 285.

32 G. Miyajima, H. Akiyama and K. Nishimoto, Org. Magn. Reson., 4 (1972) 811.

33 G.C. Levy, R.L. Lichter and G.L. Nelson, Carbon-13 Nuclear Magnetic Resonance Spectroscopy, 2nd edition, Wiley–Interscience, New York, 1980, pp. 111–112.