The evidence for second- and third-row complexes is much less compelling and here we can only speculate, keeping in mind the lack of direct structural evidence. The magnetic susceptibility data show that $Mo(mnt)_3^{2-}$ and $W(mnt)_3^{2-}$ [formally M(IV)] are diamagnetic, while $Re(mnt)_3^{2-}$ has $\mu_{eff} = 1.61$ BM, indicating one unpaired electron. These results can be accommodated either in D_3-type octahedral or trigonal-prismatic (D_{3h}) coordination.

For example, in D_3 symmetry, the diamagnetism would require that the a_1 orbital be lowest with the e orbitals of sufficiently higher energy to cause spin pairing.[28] The Re complex would then be expected to have a ^2E (orbitally degenerate) ground state. In D_{3h} symmetry, the scheme that we derived previously[6] predicts diamagnetism for the W and Mo complexes and an orbitally degenerate $^2E'$ ground state for $Re(mnt)_3^{2-}$. Thus either geometry can accommodate the observed magnetic susceptibility and electron spin resonance behavior.

The electronic spectral properties of the Mo and Re complexes are also of interest as they both show intense bands at ~15,000 and ~25,000 cm^{-1} similar to their neutral counterparts with $S_2C_2(C_6H_5)_2$ and tdt ligands. Based on our molecular orbital scheme[6] we would predict the 15,000-cm^{-1} band to be present in dianionic trigonal-prismatic complexes, but we would not expect the 25,000-cm^{-1} band to be present. To complicate matters further, the first band in the $W(mnt)_3^{2-}$ spectrum occurs at substantially higher energy than the first band in the Re or Mo complex. These results are puzzling and we shall not attempt an explanation until the structural picture is clarified.

Finally, we inspect the polarographic data for the second- and third-row complexes. The trends in the half-wave potentials appear very much like those for $M(S_2C_2(C_6H_5)_2)_3$ complexes (see Table VI). Thus the large jump in potential comes between the $(0 \rightarrow -1)$ and $(-1 \rightarrow -2)$ waves for the Re complexes, while it occurs between the $(-1 \rightarrow -2)$ and $(-2 \rightarrow -3)$ waves for the Mo and W complexes. These results indicate a qualitative similarity in electronic energy levels in the two sets of complexes and thus are not inconsistent with the possibility that the tris-mnt ones have trigonal-prismatic structures. Further structural work in this area is obviously needed.

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[28] For a helpful discussion of the situation for D_3 complexes see ref 24.

CONTRIBUTION NO. 1736 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY, BLOOMINGTON, INDIANA 47401,
AND THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS 61801

1,7-Phosphacarbollylnickel[1] Complexes Containing Allyl, Cyclopropenyl, or Nitrosyl Ligands

BY PETER S. WELCKER AND LEE J. TODD[2]

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The synthesis and characterization of 1,7-phosphacarbollylnickel complexes containing allyl, cyclopropenyl, or nitrosyl ligands are described. The asymmetry of the 1,7-phosphacarbollyl ligand is reflected in the unusual proton nmr spectra of the allyl and 2-methallyl complexes.

Stable cyclopentadienyl compounds of nickel occur in which the valence shell formally contains 18, 19, or 20 electrons. Nickelocene is a 20-electron system which can be readily oxidized to the formal Ni(III) ion, $(\pi\text{-}C_5H_5)_2Ni^+$. At lower temperature (−40°) further oxidation has been observed electrochemically to give the 18-electron ion $(\pi\text{-}C_5H_5)_2Ni^{2+}$.[3] A phosphacarborane analog of nickelocene, $(1,7\text{-}B_9H_9CHPCH_3)_2Ni$, has also been reported.[4] The mixed sandwich molecule $(C_5H_5)Ni(1,2\text{-}B_9C_2H_{11})$ has been prepared and represents an example of a stable 19-electron system.[3] Stable 18-electron bis(π-ligand)nickel(IV) molecules have been formed using the $B_{10}H_{10}CH^{3-}$ and 7,8- and $7,9\text{-}B_9C_2H_{11}^{2-}$ ions.[5,6] Although all of these ligands are

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[1] The numbering system employed in this article follows the new nomenclature rules which recently appeared in *Inorg. Chem.*, **7**, 1945 (1968). Unfortunately, two numbering systems have been suggested for *closo* transition metal complexes. One method suggests that the *nido* borane ligand be numbered prior to (rule 2.321) incorporation into the metal complex [*e.g.*, $(C_3H_5)Ni(7,9\text{-}B_9H_9CHPCH_3)$]. The other method numbers the *closo* complex considering the metal atom as part of the cage [*e.g.*, $(C_3H_5)Ni(1,7\text{-}B_9H_9CHPCH_3)$]. The latter method avoids the difficulty of translating from one numbering system to another when comparing closely related icosahedral systems. It is hoped that the nomenclature committee will rapidly clarify this numbering system ambiguity.

[2] Correspondence should be addressed to this author at the Department of Chemistry, Indiana University, Bloomington, Ind. 47401.

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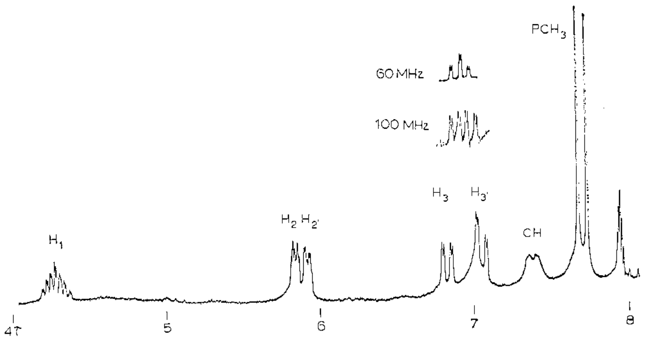

Figure 1.—The proton nmr spectrum (220 MHz) in acetone-d_6 solution of $C_3H_5Ni(1,7\text{-}B_9H_9CHPCH_3)$.

isoelectronic, the larger the negative charge on the ligands, the more stable is the derived 18-electron nickel complex.

We report here the synthesis and properties of some phosphacarbollide–nickel complexes containing allyl, nitrosyl, or cyclopropenyl ligands which are formally 18-electron systems.

Results and Discussion

Reaction of triphenylcyclopropenylnickel carbonyl bromide[7] with $7,9\text{-}B_9H_9CHPCH_3^-$ ion in tetrahydrofuran produced the crystalline red complex $C_3(C_6H_5)_3Ni(1,7\text{-}B_9H_9CHPCH_3)$ in 40% yield. The elemental analyses of this compound and others reported in the paper are given in Table I. The low-voltage mass spectrum of this compound cuts off at m/e 496 corresponding to the parent ion $^{12}C_{23}{}^{1}H_{28}{}^{11}B_9{}^{31}P^{62}Ni^+$. The most intense peak in the spectrum occurs at m/e 267 which is due to the triphenylcyclopropenyl cation. The proton nmr spectrum ($CDCl_3$ solution) contains a multiplet centered at τ 2.3 (15 H), a broad singlet at τ 8.45 (1 H), and a doublet (J = 13 cps) at τ 8.55 (3 H) which are assigned to the phenyl protons, carborane CH, and P–CH_3 function, respectively. The ^{11}B nmr spectrum at 32 MHz is complex and uninformative.

TABLE I

ANALYTICAL DATA FOR PHOSPHACARBOLLYL TRANSITION METAL DERIVATIVES

Compound	% calcd C	% calcd H	% calcd Ni	% found C	% found H	% found Ni
$C_3(C_6H_5)_3Ni(1,7\text{-}B_9H_9CHPCH_3)$	56.21	5.74	11.94	56.21	5.68	11.77
$C_3H_5Ni(1,7\text{-}B_9H_9CHPCH_3)$	22.64	6.85	22.13	22.59	6.82	22.00
$C_4H_7Ni(1,7\text{-}B_9H_9CHPCH_3)$	25.80	7.24	21.02	26.44	7.56	20.88

Allylmagnesium chloride, $7,9\text{-}B_9H_{10}CHPCH_3$, and nickel(II) chloride were allowed to react at −15° for several hours to produce the red complex $(C_3H_5)Ni(1,7\text{-}B_9H_9CHPCH_3)$ in 34% yield. The corresponding 2-methallyl complex was prepared in the same manner in 48% yield. The mass spectra of these compounds cut off at m/e 270 and 284 corresponding to the parent ions $^{12}C_5{}^{1}H_{18}{}^{11}B_9{}^{31}P^{62}Ni^+$ and $^{12}C_6{}^{1}H_{20}{}^{11}B_9{}^{31}P^{62}Ni^+$, respectively. The proton nmr of the allyl complex (acetone-d_6 solution) is shown in Figure 1. The doublet at τ 7.72 (J = 13 Hz) and the broad doublet at τ 7.4 (J = 10 Hz) are assigned to the P–CH_3 and the carborane CH, respectively. Both proton signals are probably split by spin coupling to the phosphorus nucleus. The signals attributed to the allyl group are a multiplet at τ 4.26 (H_1) (see Figure 2), a pair of doublets centered at τ 5.90 (H_2 and H_2'), and a pair of doublets at τ 6.86 and 7.08 (H_3 and H_3'). These signals are further split (2–3 Hz) by long-range spin coupling to the phosphorus atom. The temperature dependence of the proton spectrum was studied between −94 to +80° and the spectrum was found to be invariant. The 100-MHz proton nmr spectrum of the 2-methallyl complex (acetone-d_6 solution) contains a doublet (J = 12 Hz) at τ 7.70 (3 H) and a broad signal at τ 7.5 (1 H) which can be assigned to the P–CH_3 and carborane CH protons, respectively. The signals associated with the 2-methallyl group consist of a doublet (J = 1 Hz) at τ 7.82 (2-methyl), a pair of doublets at τ 6.82 (J = 4 Hz) and 7.00 (J = 3 Hz) (H_3 and H_3'), and two complex signals at 5.93 and 6.03 (H_2 and H_2'). The extra coupling associated with the H_2 and H_2' protons in the spectra of the allyl and methallyl complexes may be long-range coupling between the H_2 and H_2' protons themselves.

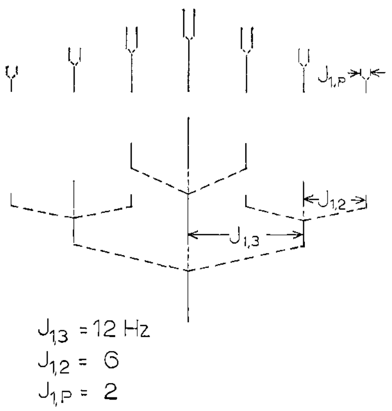

Figure 2.—Analysis of the H_1 multiplet (τ 4.26) of the proton nmr spectrum of $C_3H_5Ni(1,7\text{-}B_9H_9CHPCH_3)$. The calculated intensities of the septet peaks are 1:2:3:4:3:2:1. The observed intensities are 1:2.03:2.95:4.03:2.95:2.03:1.

The essential determining features of the allyl spectrum appear to be (a) the asymmetry of the cage which causes the two *syn* (H_2 and H_2') and the two *anti* protons (H_3 and H_3') of the allyl group to be nonequivalent (see Figure 3) and (b) the lack of completely free rotation of the allyl group.

If $7,9\text{-}B_9H_9CHPCH_3^-$ and nickel(II) chloride are mixed in tetrahydrofuran solution and then nitric oxide is bubbled into the mixture for 45 min, a low yield of red $(NO)Ni(1,7\text{-}B_9H_9CHPCH_3)$ is formed. The high-resolution mass spectrum of this compound contained a peak at m/e 257.0881 (calcd for $^{11}B_9{}^{1}H_{13}{}^{12}C_2{}^{31}P^{14}N^{16}O\text{-}{}^{60}Ni$: 257.0880). The cutoff point of the mass spectrum occurred at m/e 261 corresponding to the parent ion $^{12}C_2{}^{1}H_{13}{}^{11}B_9{}^{31}P^{14}N^{16}O^{64}Ni$. The volatility of this compound is considerably greater than that of the allyl or cyclopropenyl complexes and a considerably stronger parent ion multiplet peak was seen. Thus the 1.1% of the complex containing ^{64}Ni can be readily observed. The new complex exhibits a strong nitrosyl band in the

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(7) E. W. Gowling and S. F. A. Kettle, *Inorg. Chem.*, **3**, 604 (1964).

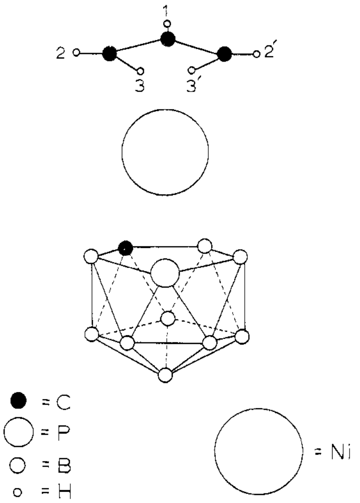

Figure 3.—The proposed structure of $C_3H_5Ni(1,7\text{-}B_9H_9CHPCH_3)$.

infrared spectrum at 1842 cm^{-1}. The analogous metallocene compound $(C_5H_5)Ni(NO)$ was prepared by Piper, Cotton, and Wilkinson[8] from nickelocene in a similar manner and this compound shows a nitrosyl infrared band at 1833 cm^{-1}. The proton nmr spectrum of the phosphacarbollylnickel nitrosyl complex ($CDCl_3$ solution) contains a sharp doublet (J = 13 Hz) at τ 7.60 (3 H) and a broad singlet at τ 8.75 (1 H) assigned to the $P\text{-}CH_3$ function and the carborane CH, respectively.

Experimental Section

Infrared spectra were measured on a Perkin-Elmer 521 or 621 instrument. Intensities of absorptions are reported as strong (s), medium (m), or weak (w). The mass spectra were obtained with either an Atlas CH-4 or an AEI MS-9 instrument. Proton nmr spectra were obtained with either a Varian A-60 or HA-100 spectrometer. The proton spectrum presented in Figure 1 was obtained on a Varian HR-220 nmr spectrometer at a field of 51.680 kg. Electronic spectra were obtained with a Cary 14 spectrometer. Elemental analyses were obtained from the University of Illinois Microanalytical Laboratory. Melting points were obtained in evacuated sealed capillaries and are uncorrected. The molecular weight determination was made using a Mechrolab Model 301A osmometer. All reactions were carried out under an atmosphere of prepurified nitrogen or argon.

$C_3(C_6H_5)_3Ni(1,7\text{-}B_9H_9CHPCH_3)$.—A 0.210-g (0.00048-mol) sample of $[C_3(C_6H_5)_3NiBr(CO)]_2$ was put into a 50-ml flask equipped with a septum and condenser. A 0.124-g (0.00075-mol) sample of $7,9\text{-}B_9H_{10}CHPCH_3$ was deprotonated with approximately 2 equiv of NaH in tetrahydrofuran solution for 1 hr and the supernatant liquid was syringed into the 50-ml reaction flask. The reaction was refluxed for 12 hr. The solvent was removed under vacuum and the residues were chromatographed on a silica gel column with benzene eluent. The first red fraction was crystallized from heptane–benzene to give 0.0940 g (40% yield) of $C_3(C_6H_5)_3Ni(1,7\text{-}B_9H_9CHPCH_3)$, red crystals, mp 202–203°.

The infrared spectrum (KBr disk) contained absorptions at λ_{max} 3060 (w), 2920 (w), 2560 (s), 1700 (w), 1620 (w), 1492 (w), 1445 (w), 1545 (w), 1080 (w), 1033 (w), 1020 (w), 980 (m), 755 (m), 685 (m), and 540 (m) cm^{-1}. The electronic spectrum (cyclohexane solution) contained absorptions at λ_{max} (ϵ) 260 (29,600), 300 (27,300), 350 (1100), and 420 (490) mμ.

$C_3H_5Ni(1,7\text{-}B_9H_9CHPCH_3)$.—A tetrahydrofuran solution of allylmagnesium chloride (*ca.* 0.012 mol) was syringed into a flask containing 0.80 g (0.006 mol) of anhydrous $NiCl_2$, maintained at −15° in an ice–salt bath. A 0.346-g (0.0024-mol) sample of $7,9\text{-}B_9H_{10}CHPCH_3$ in THF was added. The mixture was stirred for several hours during which time the temperature was raised from −15° to room temperature. The reaction mixture was evaporated to dryness under vacuum and the residue was extracted with benzene. The extract was passed through a silica gel column and eluted with benzene. The main red band was crystallized from heptane or sublimed at 85° to give 0.216 g (34% yield) of $C_3H_5Ni(1,7\text{-}B_9H_9CHPCH_3)$, mp 120–121°.

The infrared spectrum in benzene solution contained absorptions at λ_{max} 2990 (w), 2920 (w), 2560 (s), 1381 (w), 1225 (w), 1132 (w), 1089 (w), 1015 (w), 980 (m), 915 (w), 880 (w), 850 (w), 765 (w), and 730 (w) cm^{-1}. The electronic spectrum (cyclohexane solution) contained absorptions at λ_{max} (ϵ) 275 (14,000), 313 (4370), 360 (930), and 480 (138) mμ.

$C_4H_7Ni(1,7\text{-}B_9H_9CHPCH_3)$.—The methallyl complex was prepared in the same fashion as the allyl complex. The chief difference being that its lower vapor pressure makes it impossible to sublime a pure product. It is best purified by crystallization from cyclohexane to give red needles, mp 123–124°. The osmometric molecular weight (in acetone) was observed to be 272 (calcd for $C_4H_7Ni(B_9H_9CHPCH_3)$: 279). The infrared spectrum (KBr disk) has absorptions at λ_{max} 2920 (w), 2550 (s), 1426 (w), 1398 (w), 1381 (w), 1133 (w), 1086 (w), 1036 (m), 1021 (m), 981 (m), 911 (w), 833 (w), 763 (w), 728 (w), and 386 (w) cm^{-1}. The electronic spectrum (cyclohexane solution) contained absorptions at λ_{max} (ϵ) 271 (13,800), 308 (5030), 360 (1010), and 470 (147) mμ.

$(NO)Ni(1,7\text{-}B_9H_9CHPCH_3)$.—A 0.536-g (0.00315-mol) sample of $7,9\text{-}B_9H_{10}CHPCH_3$ was deprotonated with excess sodium hydride in THF solution. This solution was transferred by syringe to a flask containing 0.546 g (0.00421 mol) of anhydrous nickel(II) chloride. The reaction was allowed to proceed for 10 min and then nitric oxide was bubbled into the reaction in a hood at room temperature and atmospheric pressure for 45 min.

The reaction mixture was flushed with nitrogen and evaporated to dryness. It was chromatographed on a 100–200 mesh silica column and eluted with benzene. The red fraction was evaporated to dryness and sublimed at 65° (0.05 mm) to give 0.048 g (6% yield) of $(NO)Ni(1,7\text{-}B_9H_9CHPCH_3)$, mp 112–113°. The infrared spectrum (carbon tetrachloride solution) has absorptions at λ_{max} 2960 (w), 2930 (w), 2855 (w), 2576 (s), 1842 (s), 1270 (w), 1090 (w), 1030 (w), and 977 (w) cm^{-1}. The electronic spectrum (cyclohexane solution) contained absorptions at λ_{max} (ϵ) 285 (11,400) and 425 (499) mμ.

Acknowledgments.—The authors thank Mr. Art Clouse for the 220-MHz nmr spectrum and the National Science Foundation for support under Grant GP-10148.

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