38 *Inorganic Chemistry, Vol. 12, No. 1, 1973* W. H. Knoth

Contribution No. 1924 from the Central Research Department, Experimental Station,
E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

Triazene Complexes of Group VIII Metals

W. H. KNOTH

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Diaryltriazene complexes of rhodium, iridium, and ruthenium have been prepared. Nmr studies have shown that in most of these the triazene ligands are chelating although a few examples of bridging triazene ligands have been found. Included in these are a binuclear and a trinuclear hydride, $[Ph_2N_3Rh(H)_2]_2C_8H_{14}$ and $[Ph_2N_3Rh(H)_2]_3C_8H_{12}$.

Introduction

Diaryltriazenido anions, $R_2N_3^-$, have been known to form metal complexes for many years,[1] but very little chemistry of these complexes has been reported and there are few structure studies. Two complexes, $[Ph_2N_3Cu]_2$[2] and $[[Ph_2N_3]_2Ni]_2$,[3] have been shown to be binuclear with bridging $Ph_2N_3^-$ ligands and very short metal–metal distances. A third complex, $[Ph_2N_3]_3Co$,[4] is monomeric with chelating $Ph_2N_3^-$ ligands; all Co–N bonds are of equal length. There has also been speculation that triazenido anions can act as unidentate ligands.[5] The multiplicity of structural possibilities, particularly the implication from the $[Ph_2N_3]_3Co$ structure that triazenido anions can act as triaza-π-allyl ligands, and the paucity of chemical studies stimulated our interest in this area. Similar considerations apparently also stimulated recent work on triazenido anions by Robinson and Uttley, who have communicated preliminary results of their work.[6]

Preparations and Reactivity

Robinson and Uttley[6] treated triazenes, R_2N_3H, with triphenylphosphinemetal complexes and observed reactions in which the net effect was oxidative addition of the N–H bond to the metal atom with or without subsequent elimination of hydrogen or some other ligand.[7] In the present study, triazenido anions were used to displace halide ion from halogen-containing group VIII metal complexes as shown in eq 1–5.

$$[Ph_3P]_3RhCl + Ph_2N_3^- \rightarrow \underset{\text{I}}{[Ph_3P]_2RhN_3Ph_2} + Ph_3P + Cl^- \tag{1}$$

$$[Ph_3P]_3Ru(H)Cl + Ph_2N_3^- \rightarrow \underset{\text{II}}{[Ph_3P]_3Ru(H)N_3Ph_2} + Cl^- \tag{2}$$

$$[Ph_3P]_4RuCl_2 + Ph_2N_3^- \rightarrow \underset{\text{III}}{[Ph_3P]_2Ru[N_3Ph_2]_2} + 2Cl^- + 2Ph_3P \tag{3}$$

$$[Ph_3P]_2Ir(CO)Cl + Ph_2N_3^- \rightarrow \underset{\text{IV}}{[Ph_3P]_2Ir(CO)N_3Ph_2} + Cl^- \tag{4}$$

$$(C_8H_{12}RhCl)_2 + 2Ph_2N_3^- \rightarrow \underset{\text{V}}{2Ph_2N_3RhC_8H_{12}} + 2Cl^- \tag{5}$$

The bis(*p*-fluorophenyl)triazene analogs of I, II, IV, and V (designated IF, IIF, IVF, and VF) were prepared similarly, using bis(*p*-fluorophenyl)triazene.

Compounds I and IF resemble $[Ph_3P]_3RhCl$[8,9] in that they readily add hydrogen, carbon monoxide, methyl iodide, and oxygen. These reactions appear to be thermally irreversible. Compounds I and IF also form an adduct with ammonia but the ammonia is loosely held. These reactions are summarized in eq 6–10.

$$\underset{\text{I}}{[Ph_3P]_2RhN_3Ph_2} + H_2 \rightarrow \underset{\text{VI}}{[Ph_3P]_2Rh(H)_2N_3Ph_2} \tag{6}$$

$$[Ph_3P]_2RhN_3Ph_2 + CH_3I \rightarrow \underset{\text{VII}}{[Ph_3P]_2Rh(CH_3)(I)N_3Ph_2} \tag{7}$$

$$[Ph_3P]_2RhN_3Ph_2 + CO \rightarrow \underset{\text{VIII}}{[Ph_3P]_2Rh(CO)N_3Ph_2} \tag{8}$$

$$[Ph_3P]_2RhN_3Ph_2 + O_2 \rightarrow \underset{\text{IX}}{[Ph_3P]_2Rh(O_2)N_3Ph_2} \tag{9}$$

$$[Ph_3P]_2RhN_3Ph_2 + NH_3 \rightleftharpoons \underset{\text{X}}{[Ph_3P]_2Rh(NH_3)N_3Ph_2} \tag{10}$$

Compound VI readily transfers hydrogen to ethylene at 25°, and I is an efficient catalyst for the hydrogenation of ethylene and 1-hexene under mild conditions (25°, 1 atm).

Compounds III and IV were recovered unchanged after treatment with hydrogen or carbon monoxide at 1 atm; IV was not affected by oxygen at 1 atm. The reaction of V with carbon monoxide gave the dimeric $[(OC)_2RhN_3Ph_2]_2$ (XI).

Reactions 6–10 established that diaryltriazene–rhodium bonds can survive a variety of reactions at the rhodium atom. It was of interest next to determine whether diaryltriazenes can act as the main stabilizing ligands in hydride complexes. Compound V, $Ph_2N_3RhC_8H_{12}$, and its *p*-fluorophenyl analog, VF, were treated with hydrogen in benzene at 40 psig and 25°. Some rhodium metal formed but hydrides were also obtained in 20–50% yield. These were highly crystalline, black, moderately air-stable compounds which are formulated as $[R_2N_3Rh(H)_2]_3C_8H_{12}$ (XII and XIIF). Elemental analysis suggests the gross formula; confirmation that the C_8 fraction is still a cyclooctadiene was obtained from proton nmr analysis (integration of vinylic to methylene protons) and support for formulation as rhodium dihydrides was obtained from integration of the hydride resonance *vs.* the low-field resonances in XIIF.

Quite surprisingly, the reaction of V with hydrogen in

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(1) (a) F. P. Dwyer, *J. Amer. Chem. Soc.*, **63**, 78 (1941); (b) F. P. Dwyer and D. P. Mellor, *ibid.*, **63**, 81 (1941).

(2) I. D. Brown and J. D. Dunitz, *Acta Crystallogr.*, **14**, 480 (1961).

(3) M. Corbett and B. F. Hoskins, *Chem. Commun.*, 1602 (1968).

(4) M. Corbett and B. F. Hoskins, *J. Amer. Chem. Soc.*, **89**, 1530 (1967).

(5) C. M. Harris, B. F. Hoskins, and R. L. Martin, *J. Chem. Soc.*, 3728 (1959).

(6) (a) S. D. Robinson and M. F. Uttley, *Chem. Commun.*, 1315 (1971); (b) *J. Chem. Soc., Chem. Commun.*, 184 (1972).

(7) For example, compounds III and VIII and the bis(*p*-tolyl)triazene analog of VI were prepared by Robinson and Uttley by the reactions of $[Ph_3P]_4RuH_2$, $[Ph_3P]_3Rh(CO)H$, and $[Ph_3P]_4RhH$ with the appropriate diaryltriazene.

(8) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966). See also P. G. H. Troughton and A. C. Skapski, *Chem. Commun.*, 575 (1968).

(9) M. C. Baird, D. N. Lawson, J. T. Mague, J. A. Osborn, and G. Wilkinson, *Chem. Commun.*, 129 (1966).

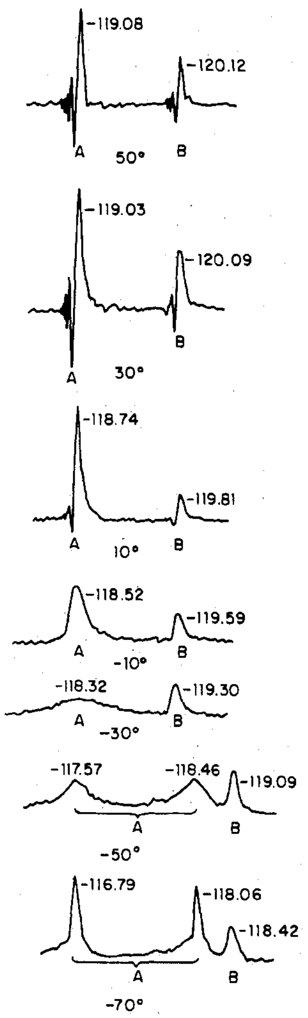

Figure 1. ^{19}F nmr spectra of $(p\text{-}FC_6H_4)_2N_3RhC_8H_{12}$ from +50 to -70° in tetrahydrofuran; ϕ in ppm from F-11.

toluene, instead of in benzene, gave a different highly crystalline black, moderately air-stable hydride, XIII. The preparation of XIII was not as reliable as that of XII; yields were generally lower and in a few attempts no XIII was obtained. Compound XIII was also obtained from a hydrogenation of V in *p*-xylene. Elemental and nmr analyses suggest that XIII is $[Ph_2N_3Rh(H)_2]_2C_8H_{14}$. The assignment of the C_8 moiety as cyclooctene is based on the observed ratio of vinylic to methylene protons in the nmr spectra.

Structural Considerations

Some major points of interest are whether the triazene ligands in the above complexes are monodentate, chelating, or bridging; whether in chelating or bridging structures the terminal nitrogen atoms are equivalent; and, finally, the identity of the structures of XII and XIII.

Compound I is prepared in tetrahydrofuran and is initially isolated as a solvate, $[Ph_3P]_2RhN_3Ph_2 \cdot 2C_4H_8O$. Desolvation by heating at 95° *in vacuo* gives monomeric $[Ph_3P]_2RhN_3Ph_2$ according to cryoscopic and ebullioscopic molecular weight determination in benzene. Recrystallization of this monomer from toluene gives a dimer (cryoscopic determination in benzene) which reverts to the monomer in refluxing benzene. Only one ^{19}F resonance is observed for monomeric IF at 80° (ϕ -119.11 ppm) or for the dimer (ϕ -121.99 ppm) at +35 to -80°. Both forms have been observed in some samples. It is inferred from the ^{19}F spectra that the terminal nitrogen atoms in the triazene ligands in I are equivalent on the nmr time scale in both the monomer and the dimer. This is consistent both with a monodentate structure in which rapid triazene ligand exchange is occurring even at -80° and with a chelate structure. The latter is preferred, not only because of the precedent set by $Co[N_3Ph_2]_3$ but also because of the fact that if I has a unidentate triazene ligand, then it has a three-coordinate rhodium atom in a 14-electron configuration. A four-coordinate 16-electron configuration is obtained simply by chelating the ligand and this seems much more reasonable.

All the other compounds reported here are monomeric except for $[(OC)_2RhN_3Ph_2]_2$ (XI) and possibly $[Ph_3P]Ru[N_3Ph_2]_2$ which was too insoluble for molecular weight determinations. The infrared spectrum of XI shows that the carbonyl groups are terminal; hence the triazene ligands must be bridging. The ^{19}F spectrum of XIF shows only one fluorine resonance from +80 to -80°, demonstrating equivalence of the terminal triazene nitrogen atoms.

The high-field proton resonance spectra of $[Ph_3P]_2Rh(H)_2N_3Ph_2$ and $[Ph_3P]_3Ru(H)N_3Ph_2$ reveal that the phosphines are cis to the hydrogen on the central metal atom but do not distinguish conclusively between five- and six-coordinate structures. The ^{19}F nmr spectra of the fluorophenyltriazene complexes are more informative. The ^{19}F spectra of $[Ph_3P]_3Ru(H)N_3(C_6H_4F)_2$ (IIF), $[Ph_3P]_2Ir(CO)N_3(C_6H_4F)_2$ (IVF), $C_8H_{12}RhN_3(C_6H_4F)_2$ (VF), $[Ph_3P]_2Rh(H)_2N_3(C_6H_4F)_2$ (VIF), and $[Ph_3P]_2Rh(CO)N_3(C_6H_4F)_2$ (VIIIF) were determined down to -70 or -80°. All except VF exhibited only one resonance even at the lower temperatures. It is inferred from this that II, IV, VI, and VIII have chelating triazene ligands and that the terminal nitrogen atoms are equivalent (triaza-π-allyl structures) on the nmr time scale. Monodentate bis(*p*-fluorophenyl)triazene ligands should exhibit two equal fluorine resonances unless rapid triazene ligand exchange is occurring. This is unlikely; the proton-decoupled ^{19}F spectrum of a mixture of $[Ph_3P]_2Ir(CO)N_3(C_6H_4F)_2$ and $[Ph_3P]_2Rh(CO)N_3(C_6H_4F)_2$ exhibited two sharp resonances with no apparent exchange broadening. Similarly, a mixture of the rhodium complex and the lithium salt of bis(*p*-fluorophenyl)triazene displayed two sharp resonances.

Molecular weight determinations suggest that $C_8H_{12}RhN_3(C_6H_4F)_2$ (VF) is monomeric in boiling benzene but contains some dimer at 5°. This is supported by the ^{19}F nmr spectrum in toluene which displays two unequal resonances. The weaker one is assigned to the dimer. As shown in Figure 1, this signal (B) is unaffected by chilling to -70° (except for a small change in chemical shift) but the other resonance (A), assigned to the monomer, collapses at -30° and reemerges as two equal resonances on further cooling. The single resonance observed for the monomer at higher temperature is interpreted in terms of a chelate structure containing a symmetrical triazene ligand. The two resonances at lower temperatures reflect nonequivalent fluorine atoms. It does not seem reasonable that cooling should convert a chelate triazene ligand to a monodentate one; furthermore the rhodium in $C_8H_{12}RhN_3(C_6H_4)_2$ would be three-coordinate with a 14-electron configuration if the triazene ligand was monodentate. This also seems unlikely. Consequently it is assumed that the triazene ligand is still chelating at the lower temperature but that the terminal nitrogen atoms have become nonequivalent. One possibility is the stabilization of a σ-π form (Figure 2) at low temperature; this has been reported for molybdenum and

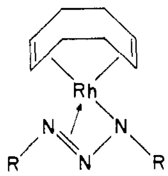

Figure 2. Low temperature limiting structure proposed for R_2N_3Rh-C_8H_{12}.

Table I. Infrared Class Assignments

Class A	Class B
$(Ph_3P)_2RhN_3Ph_2$	$(Ph_3P)_2Rh(CO)N_3Ph_2$
$(Ph_3P)_2Rh(H)_2N_3Ph_2$	$(Ph_3P)_2Ir(CO)N_3Ph_2$
$(Ph_3P)_2Rh(CH_3)(I)N_3Ph_2$	$(Ph_3P)_3Ru(H)N_3Ph_2$
$(Ph_3P)_2Ru(N_3Ph_2)_2$	$(Ph_3P)_2Rh(NH_3)N_3Ph_2$
$(Ph_3P)_2Rh(O_2)N_3Ph_2$	$(C_8H_{12})RhN_3Ph_2$
	$[(OC)_2RhN_3Ph_2]_2$
	$[Ni(N_3Ph_2)_2]_2$

tungsten complexes of the monoazaallyl ligand (p-$CH_3C_6H_4)_2C{=}NC(p$-$CH_3C_6H_4)_2^-$.[10]

The assignment of bidentate triazene structures, either bridging or chelating, to all the complexes described above contrasts with the work of Robinson and Uttley[6] in which they found evidence for both monodentate and bidentate triazene complexes. While some of their complexes, such as those of palladium and platinum, have not been prepared in this study, there is a disagreement regarding the structure of $[Ph_3P]_2Rh(CO)N_3R_2$. Robinson and Uttley have assigned a four-coordinate structure with a monodentate triazene ligand (R = phenyl) while a five-coordinate structure with a chelating triazene ligand (R = p-fluorophenyl) has been deduced from the ^{19}F studies discussed above. Although there is a possibility that the p-fluoro substituent affects the structure, this seems unlikely and it is assumed here that the phenyl and p-fluorophenyl analogs have similar structures. Robinson and Uttley have based their assignments of monodentate or bidentate triazene ligands on infrared correlations. They noted that the infrared spectra of diphenyltriazene complexes fall into one of two classes. One class, arbitrarily designated here as class A, has absorptions at *ca.* 1260-1300 and 1580-1600 cm^{-1} and this pattern was assigned by Robinson and Uttley to chelate triazene ligands. The other class, arbitrarily designated here as class B, has absorptions at *ca.* 1150, 1190-1210, 1260-1300, and 1580-1600 cm^{-1} and this pattern was correlated with monodentate triazene ligands. The absorptions that distinguish the classes are those at 1150 and 1190-1210 cm^{-1}. We find that triphenylphosphine complexes generally exhibit a weak to moderate intensity absorption at 1150 cm^{-1} which is due to the triphenylphosphine. In some complexes which contain both triazene and triphenylphosphine ligands there is an 1150-cm^{-1} band which is clearly too intense to result from the triphenylphosphine alone; in other cases the assignment of the 1150-cm^{-1} band is not so easy. The 1190-1210-cm^{-1} absorption would therefore appear to be the more reliable criterion for assignment of such a complex to class A or class B. In Table I there is a list of most of the complexes described in this paper, as well as $[Ni(N_3Ph_2)_2]_2$, broken down into class A or class B assignments. All of the complexes in class B have absorption bands at 1190-1210 and at 1150-1160 cm^{-1}. None of those in class A have absorption at 1190-1210 cm^{-1}. The assignments of $(Ph_3P)_2$-$Rh(H)_2N_3Ph_2$ and $(Ph_3P)_2Ru(N_3Ph_2)_2$ to class A and of $(Ph_3P)_2Rh(CO)N_3Ph_2$ to class B are consistent with Robinson and Uttley's structural assignments for these complexes or their 1,3-bis(p-tolyl)triazene analogs. The $[Ni$-$(N_3Ph_2)_2]_2$ was prepared according to the literature[1b,5] and the infrared spectrum was determined in the present work. The full infrared spectra of this complex (class B), of $(Ph_3$-$P)_2Rh(CO)N_3Ph_2$ (Class B), and of $(Ph_3P)_2Rh(O_2)N_3Ph_2$ (class A) are shown in Figures 3-5 respectively.

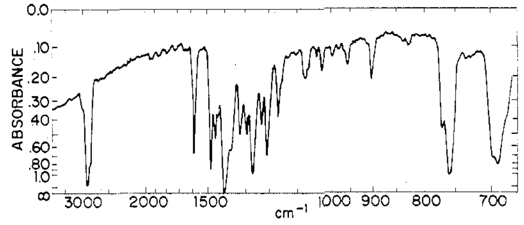

Figure 3. Infrared spectrum (Nujol mull) of $[Ni(N_3Ph_2)_2]_2$.

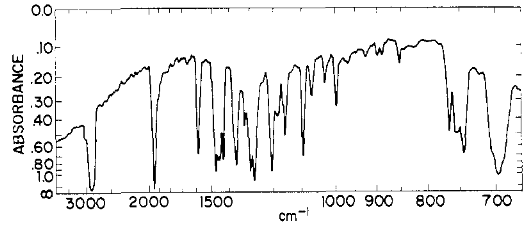

Figure 4. Infrared spectrum (Nujol mull) of $(Ph_3P)_2Rh(CO)N_3Ph_2$.

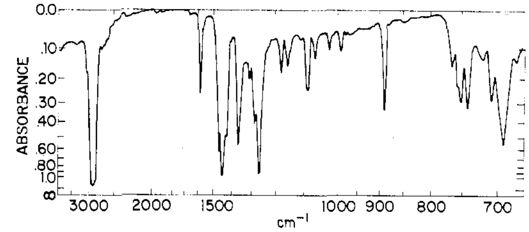

Figure 5. Infrared spectrum (Nujol mull) of $(Ph_3P)_2Rh(O_2)N_3Ph_2$.

Robinson and Uttley's infrared correlation stipulates that all class B spectra should contain unidentate triazene ligands. However, it is known from X-ray analysis that the triazene ligands in $[Ni(N_3Ph_2)_2]_2$ are bidentate (bridging), and the dimeric nature of $[(OC)_2RhN_3Ph_2]_2$ requires that they be bridging in this complex also because the carbonyl groups are terminal. Furthermore, if the triazene ligands in C_8H_{12}-RhN_3Ph_2 and in $[(OC)_2RhN_3Ph_2]_2$ were unidentate, then, as discussed above, these complexes would have rhodium in an unlikely three-coordinate 14-electron configuration. While the square-planar structures with monodentate triazene ligands assigned to $[Ph_3P]Pd(N_3R_2)_2$ and $[Ph_3P]_2Pt$-$(N_3R_2)_2$ by Robinson and Uttley may be correct, the infrared basis for these assignments does not appear to be reliable. Their nmr data[6b] are compatible with symmetrical chelate structures at higher temperatures and stabilized σ-π forms at lower temperatures.

The high-field proton magnetic resonance spectrum of $[Ph_2N_3Rh(H)_2]_3C_8H_{12}$ (XII) at 220 MHz is shown in Figure 6. All hydridic protons are equivalent and appear to be coupling with three rhodium atoms: a set of one and a set of two. A fresh solution of the p-fluorophenyl analog in methylene chloride displays one fluorine resonance but additional resonances develop fairly soon on aging. It is proposed that this trinuclear complex has the structure shown in Figure 7 in which the triazene ligands bridge a triangle of rhodium atoms with the cyclooctadiene above the plane of this triangle. The cyclooctadiene may be "spinning" so as

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[10] H. R. Keable and M. Kilner, *Chem. Commun.*, 349 (1971).

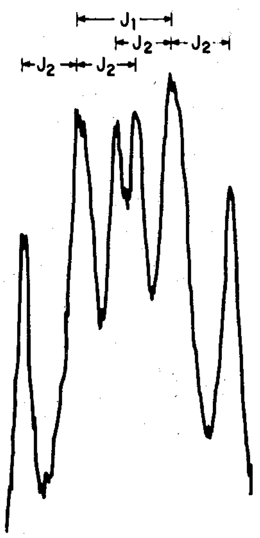

Figure 6. High-field ^1H nmr spectrum of $[Ph_2N_3Rh(H)_2]_3C_8H_{12}$ at 220 MHz in toluene, δ –16.9; J_1 = 23 Hz; J_2 = 13 Hz.

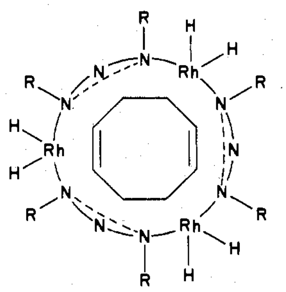

Figure 7. Proposed structure of $[R_2N_3RhH_2]_3C_8H_{12}$; R = C_6H_5 or p-FC_6H_4.

to share its π electrons equally with all three rhodium atoms, thus making them equivalent. This "spinning" could be aided by the electron deficiency of the molecule as a whole; it is two electrons short of the 48 required for each rhodium atom to have a 16-electron configuration. Precedents for this proposed structure include $(C_5H_5)_4Rh_3H$ in which a C_5H_5 ring is shared equally by three rhodium atoms, which form an almost equilateral triangle,[11] and $PhCCo_3(CO)_6$-C_8H_8 in which cyclooctatetraene is bonded (*via* three of its double bonds) to a triangle of cobalt atoms.[12] The hydridic protons in the proposed structure for XII are assumed to couple differently with the rhodium atom to which they are directly bonded than with the other two rhodium atoms to arrive at the observed spectrum.

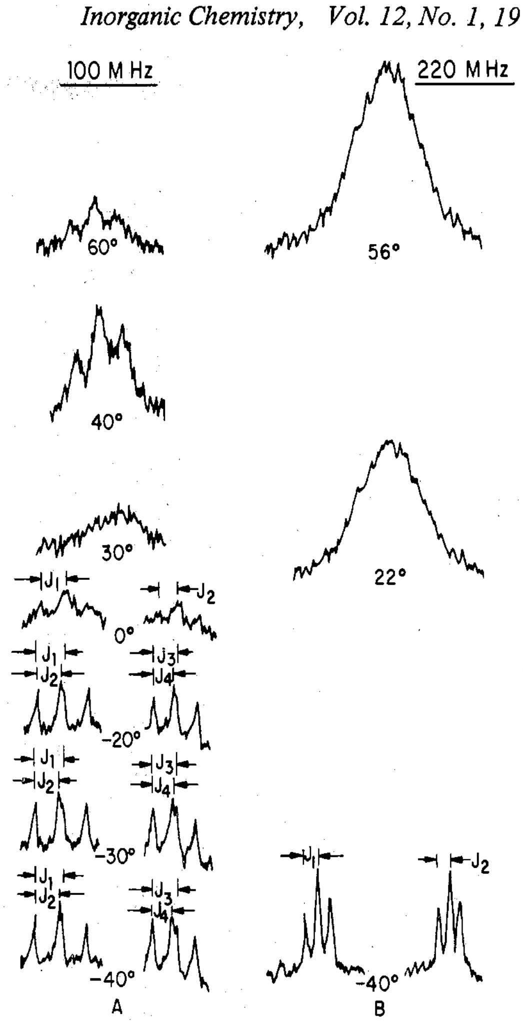

Figure 8. High-field ^1H nmr spectra of $[Ph_2N_3RhH_2]_2C_8H_{14}$ in toluene

	100 MHz		220 MHz	
Temp, °C	δ, ppm	J, Hz	δ, ppm	J, Hz
60	–18.7	25		
56			–18.6	
40	–18.7	25		
30	–18.6			
22			–19.4	
0	–17.7	J_1 = 25		
	–20.0	J_2 = ∿24		
–20	–17.7	J_1 = 30, J_2 = 26		
	–20.0	J_3 = 26, J_4 = 22		
–30	–17.7	J_1 = 29, J_2 = 25		
	–20.0	J_3 = 25, J_4 = 21		
–40	–17.7	J_1 = 30, J_2 = 26	–17.4	J_1 = 27
	–20.0	J_3 = 26, J_4 = 21	–19.7	J_2 = 22

The high-field proton magnetic resonance spectrum of $[(C_6H_5)_2N_3Rh(H)_2]_2C_8H_{14}$ (XIII) at 22° in toluene is a broad peak at 220 MHz; on cooling, the resonance collapses and reemerges as two triplets which are equal in area but not in coupling constants (Figure 8B). At 100 MHz these triplets are seen to be closely spaced doublets (Figure 8A). As with XII it is believed that only rhodium–hydrogen and no hydrogen–hydrogen coupling is being observed. Also, in common with XII, the composition of XIII leaves the molecule two electrons short of that required for each rhodium atom to have a 16-electron configuration. It is proposed that XIII has a structure similar to that of XII except that XIII is binuclear instead of trinuclear and has coordinated cyclohexene in place of cyclohexadiene. The nmr equivalence of the hydridic protons in XIII at higher temperatures requires that the cyclooctene oscillate rapidly between the two rhodium atoms (or bridge them); the nonequivalent proton sets observed at low temperatures require that the exchange of the cyclooctene between the two rhodium atoms be much slower under these conditions. Structures with hydrogen bridging the two rhodium atoms seem less reasonable.

Experimental Section

The ^1H spectra were determined on a Varian HR-220 or a Varian HA-100 spectrometer. The ^{19}F spectra were determined at 94.1 MHz on a Varian HA-100 spectrometer with proton noise decoupling by a Varian V4311 unit and are referenced to internal Freon F-11. All chemical shifts are reported with the upfield direction increasingly negative. Diphenyltriazene was purchased from Eastman Organic Chemicals; bis(p-fluorophenyl)triazene was

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(11) E. O. Fischer, O. S. Mills, E. F. Paulus, and H. Wawersik, *Chem. Commun.*, 645 (1967).

(12) B. H. Robinson and J. Spencer, *J. Organometal. Chem.*, 33, 97 (1971).

prepared by adapting a literature preparation[13] of diphenyltriazene.

$(Ph_3P)_2RhN_3Ph$ and $(Ph_3P)_2RhN_3(C_6H_4F)_2$. A solution of *n*-butyllithium in hexane (45 ml, 1.6 *M*, 7.2 mmol) was added to 1,3-diphenyltriazene (1.5 g, 7.6 mmol) in tetrahydrofuran (200 ml). After 1 min, $(Ph_3P)_3RhCl$[8] (6 g, 6.5 mmol) was added. The reaction mixture was stirred for 5 min. Filtration gave a small amount of solid which was discarded. The filtrate was allowed to stand for 16 hr and was then refiltered to obtain 1.94 g (31%) of $(Ph_3P)_2RhN_3Ph_2 \cdot 2C_4H_8O$ as a crystalline red solid. Concentration of the filtrate to about 40 ml afforded an additional 2.85 g (46.5%, total yield 77.5%) of the same product (dec pt 164–184°). Proton nmr confirmed the presence of 2 equiv of tetrahydrofuran. *Anal.* Calcd for $C_{56}H_{56}N_3O_2P_2Rh$: C, 69.48; H, 5.83; N, 4.34; O, 3.30; P, 6.40; mol wt 968. Found: C, 69.94, 69.48; H, 5.76, 5.49; N, 4.79, 4.59; O, 3.05, 3.10; P, 6.79; mol wt 946, (boiling point in THF).

Desolvation of $(Ph_3P)_2RhN_3Ph_2 \cdot 2C_4H_8O$ was accomplished by two procedures. A mixture of methylcyclohexane (25 ml) and $(Ph_3P)_2RhN_3Ph_2 \cdot 2C_4H_8O$ (0.5 g) was refluxed in a nitrogen atmosphere for 2 hr. Filtration of the hot mixture gave 0.3 g of a red solid which contained no tetrahydrofuran detectable by infrared analysis. The analytical sample was recrystallized from toluene; molecular weight determinations showed it to be a dimer. *Anal.* Calcd for $[C_{48}H_{40}N_3P_2Rh]_2$: C, 69.98; H, 4.89; N, 5.10; O, 0.0; mol wt 1648. Found: C, 69.92; H, 4.98; N, 5.08; O, 0.33; mol wt 1533 (freezing point in benzene).

Another sample of $(Ph_3P)_2RhN_3Ph_2 \cdot 2C_4H_8O$ was heated at 95° *in vacuo* for 19 hr. Proton nmr confirmed complete removal of tetrahydrofuran. The molecular weight in benzene was found to be 792 (boiling point) and 857 (freezing point) suggesting a monomeric formulation (calcd 824). A similarly prepared sample was recrystallized from toluene. Molecular weight determinations gave values of 1503 (freezing point) and 850 (boiling point), suggesting dimerization had occurred during the recrystallization and that dissociation had occurred on heating.

The preparation of $(Ph_3P)_2RhN_3(C_6H_4F)_2$ was conducted in the same fashion using bis(*p*-fluorophenyl)triazene except that it was necessary to concentrate the reaction mixture filtrate to about 30 ml before the product would crystallize from the solution. The yield of the tetrahydrofuran solvate was 7.8 g, 60%, in a run that was twice the scale of the above. Desolvation was accomplished by heating the solvate 30 min in boiling methylcyclohexane; filtration of the hot mixture gave the pure material, mp 181–183°. *Anal.* Calcd for $C_{48}H_{38}F_2N_3P_2Rh$: C, 67.06; H, 4.46; F, 4.42; P, 7.21; mol wt 860 Found: C, 66.32, 66.06; H, 4.35, 4.44; F, 3.85; P, 7.16; mol wt 891 (freezing point in benzene), 1014 (boiling point in benzene).

The proton-decoupled ^{19}F resonance of $(Ph_3P)_2RhN_3(C_6H_4F)_2$ in toluene at 80° consisted of a singlet at -119.11 ppm (high field) from F-11. At 35° the resonance was at -121.99 ppm and at -80° it was at -121.00 ppm. One sample had two resonances at +35°, one at -121.72 ppm and a smaller one at -118.90 ppm. This may reflect the presence of both monomer and dimer.

Hydrogenations with $(Ph_3P)_2Rh(N_3Ph_2)$. 1-Hexene. A mixture of tetrahydrofuran (25 ml), 1-hexene (5 ml), and $(Ph_3P)_2RhN_3Ph_2 \cdot 2C_4H_8O$ (0.1 g) was stirred in a 100-ml glass pressure bottle under 46 psig of hydrogen pressure. After 3 hr the pressure was 20 psig. The bottle was repressured and stirring was continued for 16 hr. The pressure then was below 1 atm (280 mm). Analysis of the solution showed the presence of both hexene and hexane.

Ethylene. A solution of $(Ph_3P)_2Rh(N_3Ph_2) \cdot 2C_4H_8O$ (0.1 g) in tetrahydrofuran (25 ml) was charged to a 100-ml glass pressure bottle which was chilled and evacuated. It was pressured to 8 psig with hydrogen and then to 23 psig with ethylene, warmed to room temperature, and stirred for 18 hr. The pressure dropped to 2 psig. Analysis of the gas phase showed that it contained ethane and ethylene in a 55:1 ratio.

$(Ph_3P)_2Rh(N_3Ph_2)O_2$. Air was bubbled through a solution of $(Ph_3P)_2RhN_3Ph_2 \cdot 2C_4H_8O_2$ (0.1 g, 0.1 mmol) for 30 min. The addition of petroleum ether (bp 38–49.6°) precipitated a yellow solid (A) which was removed by filtration. A crystalline yellow solid (B) separated slowly from the filtrate. Both A and B analyzed for $(Ph_3P)_2Rh(N_3Ph_2)O_2$ despite a noticeable difference between their infrared spectra. The infrared spectrum of B exhibited a sharp band at 890 cm^{-1}, characteristic of oxygen complexes, while that of A had only a weak broad absorption in this region. *Anal.* Calcd for $C_{48}H_{40}N_3P_2O_2Rh$: C, 67.37; H, 4.71; N, 4.91; O, 3.73. Found (A): C, 67.41, 67.04; H, 4.84, 4.90; N, 4.78, 4.72; O, 4.03. Found (B): C, 67.71; H, 4.90; N, 4.95; O, 3.52.

$(Ph_3P)_2Rh(N_3Ph_2)H_2$ and $(Ph_3P)_2RhN_3(C_6H_4F)_2H_2$. Hydrogen was bubbled through a solution of $(Ph_3P)_2RhN_3Ph_2 \cdot 2C_4H_8O_2$ (2 g, 2.1 mmol) in tetrahydrofuran (50 ml) for 40 min. The resulting yellow solution was partially concentrated. Dilution of the concentrate with hexane gave $(Ph_3P)_2Rh(N_3Ph_2)H_2$ as a bright yellow solid (1.70 g, 100%), dec pt 174–177°. *Anal.* Calcd for $C_{48}H_{42}N_3P_2Rh$: C, 69.81; H, 5.12; N, 5.08; P, 7.50; Rh, 12.46; mol wt 826. Found: C, 70.38, 70.31; H, 5.32, 5.38; N, 5.92, 5.12; P, 7.37; Rh, 12.75; mol wt 630 (freezing point in benzene).

The proton nmr spectrum in deuteriobenzene included a hydride resonance at δ −18.4 which consisted of a quartet, consistent with equivalent hydridic hydrogen atoms split by coupling with two equivalent phosphorus atoms and the rhodium atom (J_{H-Rh} = 16 Hz, J_{H-P} = 16 Hz).

Repeating this preparation, starting with the dimer, $[(Ph_3P)_2RhN_3Ph_2]_2$ (see above), gave the same dihydride, mol wt 743.

A similar reaction with $(Ph_3P)_2RhN_3(C_6H_4F)_2$ gave $(Ph_3P)_2RhN_3(C_6H_4F)_2H_2$, dec pt 168–172°, in 80% yield. *Anal.* Calcd for $C_{48}H_{40}F_2N_3P_2Rh$: C, 66.90; H, 4.68; N, 4.88; mol wt 862. Found: C, 67.36; H, 4.91; N, 4.58.

The proton-decoupled ^{19}F nmr spectrum in toluene at 35° consisted of one resonance, at −122.60 ppm (high field) from F-11. No additional resonances appeared from −70 to +70°. The hydride resonance was the same as that of $(Ph_3P)_2Rh(N_3Ph_2)H_2$.

Hydrogen was not evolved on heating $(Ph_3P)_2Rh(N_3Ph_2)H_2$ *in vacuo* at 100–115° for 16 hr. Solutions of the dihydride in benzene and in tetrahydrofuran were refluxed without causing hydrogen loss.

Passing air through a solution of $(Ph_3P)_2Rh(N_3Ph_2)H_2$ for 5 min had essentially no effect.

A solution of $(Ph_3P)_2Rh(N_3Ph_2)H_2$ (0.5 g, 0.6 mmol) in tetrahydrofuran (20 ml) was stirred in a glass pressure bottle at 50 psig ethylene overnight at ambient temperature. The reaction mixture darkened. Partial concentration of the product solution, followed by dilution with hexane, gave 0.44 g (76%) of $(Ph_3P)_2Rh(N_3Ph_2) \cdot 2C_4H_8O$.

$(Ph_3P)_2Rh(N_3Ph_2)CO$ and $(Ph_3P)_2RhN_3(C_6H_4F)_2CO$. Carbon monoxide was passed through a solution of $(Ph_3P)_2RhN_3Ph_2 \cdot 2C_4H_8O$ (1.5 g, 1.5 mmol) in tetrahydrofuran (50 ml). The color of the solution rapidly turned from red to yellow. The yellow solution was filtered; the filtrate was concentrated and the concentrate was diluted with hexane to obtain $(Ph_3P)_2Rh(N_3Ph_2)CO$ (0.9 g, 68%), dec pt 167–173°. *Anal.* Calcd for $C_{49}H_{40}ON_3P_2Rh$: C, 69.09; H, 4.73; O, 1.87; N, 4.93; P, 7.27; Rh, 12.08; mol wt 852. Found: C, 69.24, 69.53; H, 4.81, 4.82; O, 2.45, 2.25; N, 4.97, 4.70; P, 7.28; Rh, 12.20; mol wt 770 (freezing point in benzene).

The infrared spectrum included a strong C≡O stretch at 1950 cm^{-1}.

A similar reaction with $(Ph_3P)_2RhN_3(C_6H_4F)_2$ gave $(Ph_3P)_2Rh[N_3(C_6H_4F)_2]CO$ in 85% yield, dec pt 197–211°. *Anal.* Calcd for $C_{49}H_{38}F_2N_3P_2RhO$: C, 66.30; H, 4.31; N, 4.73; O, 1.80; P, 6.98; mol wt 888. Found: C, 66.15; H, 4.30; N, 4.48; O, 2.61; P, 7.09; mol wt 819 (freezing point in benzene).

A single ^{19}F resonance is observed from −70 to +35°. In toluene this is at −123.20 ppm; in tetrahydrofuran it is at −124.08 ppm. A mixture of $(Ph_3P)_2Rh[N_3(C_6H_4F)_2]_2CO$ and $(Ph_3P)_2Ir[N_3(C_6H_4F)_2]_2CO$ in toluene exhibits sharp resonances at −122.90 and −123.32 ppm; a mixture of the former and $LiN_3(C_6H_4F)_2$ in tetrahydrofuran exhibits sharp resonances at −124.29 and −124.16 ppm. The latter in tetrahydrofuran displays a resonance at −123.99 ppm.

$(Ph_3P)_2Rh(N_3Ph_2)(CH_3)I$. A mixture of methyl iodide (20 ml) and $(Ph_3P)_2RhN_3Ph_2 \cdot 2C_4H_8O$ (2 g, 2.1 mmol) was stirred for 1 hr. Evaporation of excess methyl iodide left a gum which was transformed into a yellow solid (1.94 g) by heating in hexene. Recrystallization of this 97% yield of crude $(Ph_3P)_2Rh(N_3Ph_2)(CH_3)I$ from methylcyclohexane–benzene gave 0.75 g (37.5%) of the pure material, dec pt 182–186°. *Anal.* Calcd for $C_{49}H_{43}IN_3P_2Rh$: C, 60.94; H, 4.48; N, 4.35; I, 13.14; mol wt 966. Found: C, 61.19, 61.40; H, 4.63, 4.62; N, 3.96; I, 13.51; mol wt 866 (freezing point in benzene).

The proton nmr spectrum in deuteriochloroform included a triplet of doublets at δ 1.85, confirming the presence of a methyl group on rhodium (J_{P-H} = 7 Hz, J_{Rh-H} = 3 Hz).

$(Ph_3P)_2Rh(N_3Ph_2)NH_3$. A mixture of $(Ph_3P)_2RhN_3Ph_2$ (0.5 g, 0.6 mmol) and toluene (20 ml) was stirred in a glass pressure bottle under ammonia pressure (30 psig). A clear light yellow solution formed slowly. Dilution of the solution with hexane caused the slow separation of orange $(Ph_3P)_2Rh(N_3Ph_2)NH_3$ (0.43 g, 84%; mp data: reddens at 110–112° (NH_3 loss?), melts at 208–211° with decomposition). *Anal.* Calcd for $C_{48}H_{43}N_4P_2Rh$: C, 68.57; H, 5.15; N, 6.66; P, 7.36; mol wt 840. Found: C, 66.65, 66.60; H,

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[13] "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 163.

5.19, 5.22; N, 6.17; P, 7.12; mol wt 579 (freezing point in benzene).

The low molecular weight may result from ammonia dissociation. The ammonia is loosely held. Dissolution of the ammonia complex in tetrahydrofuran followed by reprecipitation with hexane gave a mixture of the ammonia complex and $(Ph_3P)_2Rh(N_3Ph_2)\cdot 2C_4H_8O$.

$(Ph_3P)_3Ru(H)N_3Ph_2$ and $(Ph_3P)_3Ru(H)N_3(C_6H_4F)_2$. A solution of *n*-butyllithium in hexane (4.5 ml, 1.6 *M*, 7.2 mmol) was added to diphenyltriazene (1.5 g, 7.6 mmol) in tetrahydrofuran (200 ml) in a nitrogen atmosphere. The mixture was stirred for 3 min and filtered followed by the addition of $(Ph_3P)_3RuHCl\cdot C_6H_5CH_3$[14] (6 g, 5.9 mmol) to the filtrate. Refiltration after 2 hr gave very little solid. Concentration *in vacuo* left a dark gummy residue which was transformed to an orange-red solid by heating in hexane. Recrystallization of this from benzene–hexane gave $(Ph_3P)_3Ru(H)N_3Ph_2$ as orange-red crystals (3.2 g, 50%, dec pt 189–200°). *Anal.* Calcd for $C_{66}H_{56}N_3P_3Ru$: C, 73.04; H, 5.2; N, 3.87; P, 8.56; Ru, 9.31; mol wt 1085. Found: C, 73.66, 73.62; H, 5.33, 5.47; N, 3.85; P, 8.26; Ru, 9.70; mol wt 837 (freezing point in benzene).

The high-field ^1H nmr spectrum in toluene consisted of a quartet at δ −17.2, J_{P-H} = 24 Hz.

This preparation was repeated using bis(*p*-fluorophenyl)triazene to prepare $(Ph_3P)_3Ru(H)N_3(C_6H_4F)_2$ in 77% crude yield and 39% yield of recrystallized product, mp 121–123°. *Anal.* Calcd for $C_{66}H_{54}F_2N_3P_3$: C, 70.70; H, 4.85; F, 3.39; N, 3.75; P, 8.29; mol wt 1121. Found: C, 70.81; H, 4.95; F, 3.18; N, 3.96; P, 8.12; mol wt 1250 (boiling point in benzene).

The proton-decoupled ^{19}F nmr spectrum in tetrahydrofuran (tube sealed under vacuum) consists of a sharp resonance at −113.1 ppm (high field) from F-11.

The hydride resonance of $(Ph_3P)_3Ru(H)N_3(C_6H_4F)_2$ was the same as that of its deiphenyltriazene analog.

$(Ph_3P)_2Ru(N_3Ph_2)_2$. A solution of *n*-butyllithium in hexane (7.5 ml, 1.6 *M*, 12 mmol) was added to 1,3-diphenyltriazene (2.5 g, 12.7 mmol) in tetrahydrofuran (200 ml) in a nitrogen atmosphere. After a brief period of stirring, $(Ph_3P)_4RuCl_2$ (6 g, 4.9 mmol) was added. The mixture was stirred 10 min, refluxed 20 min, and filtered hot to obtain $(Ph_3P)_2Ru(N_3Ph_2)_2$ (2.4 g, 49%) as a red crystalline solid. An additional 0.77 g (16%) separated from the filtrate on cooling and an additional 0.36 g (7.3%, total yield 72.3%) was obtained by dilution of the final filtrate with hexane. The infrared spectra of these fractions were all identical. The product decomposes at 187°. The analytical sample was dried at 135° for 4 hr *in vacuo*. *Anal.* Calcd for $C_{60}H_{50}N_6P_2Ru$: C, 70.78; H, 4.95; N, 8.25; Cl, 0.0. Found: C, 70.26, 70.41; H, 5.02, 5.07; N, 8.26; Cl, 0.0.

$(Ph_3P)_2Ir(CO)N_3Ph_2$ and $(Ph_3P)_2Ir(CO)N_3(C_6H_4F)_2$. A solution of *n*-butyllithium in hexane (6 ml, 1.6 *M*, 9.6 mmol) was added, in a nitrogen atmosphere, to 1,3-diphenyltriazene (2 g, 10 mmol) in tetrahydrofuran (150 ml). The mixture was stirred briefly and $(Ph_3P)_2Ir(CO)Cl$ (6.5 g, 8.3 mmol) was added followed by a 15-min reflux period. The mixture was filtered and the filtrate was evaporated, leaving a viscous residue which was transformed into an orange solid by heating in hexane. Recrystallization from benzene–hexane gave $(Ph_3P)_2Ir(CO)N_3Ph_2$, mp 156–158° (5.0 g, 64%). *Anal.* Calcd for $C_{49}H_{40}IrN_3OP_2$: C, 62.54; H, 4.28; N, 4.46; O, 1.70; P, 6.58; Cl, 0.0; mol wt 941. Found: C, 63.01, 63.13; H, 4.50, 4.471; N, 4.56; O, 1.58; P, 6.30; Cl, 0.0; mol wt 880 (freezing point in benzene).

Repeating the preparation of $(Ph_3P)_2Ir(CO)N_3Ph_2$ with bis(*p*-fluorophenyl)triazene gave $(Ph_3P)_2Ir(CO)N_3(C_6H_4F)_2$ in 78% yield, mp 181–189° (darkens at 174–179°). *Anal.* Calcd for $C_{49}H_{38}F_2IrN_3OP_2$: C, 60.24; H, 3.92; F, 3.80; P, 6.34; mol wt 977. Found: C, 60.31, 60.17; H, 3.40, 3.86; F, 3.79; P, 6.35; mol wt 890 (freezing point in benzene).

The ^{19}F spectrum in toluene consisted of a single resonance at −122.81 ppm (high field) from F-11 at 35°; no significant change occurred on cooling to −80°.

$Ph_2N_3RhC_8H_{12}$ and $(FC_6H_4)_2N_3RhC_8H_{12}$. A solution of *n*-butyllithium in hexane (16 ml, 1.6 *M*, 25.6 mmol) was added to 1,3-diphenyltriazene (5.0 g, 25.4 mmol) in tetrahydrofuran (200 ml). After 1 min of stirring, $(C_8H_{12}RhCl)_2$ (8.2 g, 16.6 mmol) was added. The mixture was refluxed for 30 min, filtered, and allowed to cool. Red crystals of $C_8H_{12}RhN_3Ph_2$ (6.1 g, 59%; dec pt 175–182°) separated; an additional 1.6 g (15.5%) was obtained by dilution of the filtrate with hexane. *Anal.* Calcd for $C_{20}H_{22}N_3Rh$: C, 58.97; H, 5.44; N, 10.31; Rh, 25.24; mol wt 407. Found: C, 59.07, 58.81; H, 5.69, 5.67; N, 10.31, 10.15; Rh, 25.24; mol wt 403 (boiling point in benzene).

A similar preparation with bis(*p*-fluorophenyl)triazene gave $(FC_6H_4)_2N_3RhC_8H_{12}$ in 60% yield. *Anal.* Calcd for $C_{20}H_{20}F_2N_3Rh$: C, 54.19; H, 4.55; N, 9.48; F, 8.57; Rh, 23.21; mol wt 443. Found: C, 53.90; H, 4.67; N, 9.45; F, 7.90; Rh, 23.33; mol wt 596 (freezing point in benzene), 485 (boiling point in benzene).

The ^{19}F nmr spectrum is shown in Figure 1.

$[Ph_2N_3Rh(CO)_2]_2$ and $[(p\text{-}FC_6H_4)_2N_3Rh(CO)_2]_2$. A mixture of $Ph_2N_3RhC_8H_{12}$ (3 g, 7.5 mmol) and benzene (50 ml) was charged to a glass pressure bottle. The contents were stirred under 40 psig carbon monoxide pressure at ambient temperature until a dark red solution formed. The mixture was filtered. Evaporation of the filtrate left a residue which was recrystallized from methylcyclohexane at −40° and then from hexane at normal temperature. The yield of $[Ph_2N_3Rh(CO)_2]_2$ was 1.25 g, 47%. *Anal.* Calcd for $C_{28}H_{20}N_6O_4Rh_2$: C, 47.34; H, 2.83; N, 11.83; O, 9.01; mol wt 710. Found: C, 47.85; H, 2.85; N, 11.99; O, 8.78; mol wt 744 (freezing point in benzene).

The infrared spectrum exhibited a terminal C≡O absorption (multiplet) at 2000–2100 cm^{-1}. No bridging carbonyl was apparent.

A similar reaction with $(p\text{-}FC_6H_4)_2N_3RhC_8H_{12}$ gave $[(p\text{-}FC_6H_4)_2N_3Rh(CO)_2]_2$, mp 154–156°, in 58% yield. *Anal.* Calcd for $C_{14}H_8F_2N_3O_2Rh$: C, 42.99; H, 2.06; N, 10.74; mol wt 782. Found: C, 43.45; H, 2.34; N, 10.81; mol wt 747 (freezing point in benzene).

The ^{19}F nmr spectrum in toluene consists of a single resonance from +80 to −80°; at 35° it is at −117.30 ppm (high field) from F-11.

$Ph_2N_3Rh(C_8H_{12})NH_3$. A pressure bottle containing $Ph_2N_3RhC_8H_{12}$ (3.3 g, 7.3 mmol) and benzene (30 ml) was pressured with ammonia (22 psig) and stirred for 2 hr. Filtration gave 0.37 g of a mixture of recovered $Ph_2N_3RhC_8H_{12}$ and product. The filtrate was diluted with hexane and refiltered after 1 hr to obtain 1.85 g of impure $C_8H_{12}Rh(N_3Ph_2)NH_3$. The infrared spectrum included a weak N–H absorption and differed significantly from that of $Ph_2N_3RhC_8H_{12}$. *Anal.* Calcd for $C_{20}H_{25}N_4Rh$: C, 56.60; H, 5.93; N, 13.20; Rh, 24.25. Found: C, 57.27; H, 5.75; N, 11.93; Rh, 25.22. Heating the product to 100° *in vacuo* for 5 hr converted it to $Ph_2N_3RhC_8H_{12}$.

$[Ph_2N_3Rh(H)_2]_3C_8H_{12}$. A mixture of $Ph_2N_3RhC_8H_{12}$ (4.0 g, 9.8 mmol) and benzene (65 ml) in a glass pressure bottle (320 ml) was stirred at an initial hydrogen pressure of 40 psig. The pressure fell to below atmospheric in several hours; the bottle was repressured and stirred overnight. The pressure again fell to below 1 atm. The mixture was filtered under nitrogen; the filtrate was recrystallized from toluene (10 ml) to obtain black crystalline $[Ph_2N_3Rh(H_2)]_3C_8H_{12}$ (1.4 g, 42%) which was dried at 125° *in vacuo* before analysis, mp 201–203°. *Anal.* Calcd for $C_{44}H_{48}N_9Rh_3$: C, 52.24; H, 4.78; N, 12.46; Rh, 30.52; mol wt 1012. Found: C, 52.58, 52.26; H, 4.44, 4.42; N, 12.59, 12.50; Rh, 31.53; mol wt 578 (freezing point in benzene).

Solution molecular weights (freezing point in benzene) have varied from 578 to 1960 with an average value of 1230. This may reflect instability in solution; the ^{19}F nmr of the fluorophenyl analog changes as its solutions age and the molecular weight discrepancies are considered to be artifacts. The calculated aromatic:vinylic:methylene proton ratio is 30:4:8; a fresh chloroform solution of $[Ph_2N_3Rh(H)_2]_3C_8H_{12}$ exhibits a ratio of 30:4:9.2.

$[Ph_2N_3Rh(H)_2]_2C_8H_{14}$. A pressure bottle containing $Ph_2N_3RhC_8H_{12}$ (4.0 g, 9.8 mmol) and toluene (65 ml) was stirred at an initial hydrogen pressure of 40 psig for 24 hr. The pressure dropped during this period and the bottle was repressured once. The reaction mixture was filtered to remove rhodium metal. The filtrate was evaporated and the residue was recrystallized from benzene in a nitrogen atmosphere to obtain 0.6 g (8.6%) of $[Ph_2N_3Rh(H)_2]_2C_8H_{14}$, mp 177–178°, which was dried at 60° *in vacuo*. This reaction was more erratic than the analogous one in benzene; occasionally no product was obtained. *Anal.* Calcd for $C_{32}H_{36}N_6Rh_2$: C, 54.02; H, 5.38; N, 11.81; Rh, 28.79; mol wt 711. Found: C, 54.69, 54.56; H, 5.17, 5.14; N, 12.63, 12.48; Rh, 29.16; mol wt 1000 (freezing point in benzene).

The aromatic:vinylic:methylene proton ratio observed in the nmr spectrum of $[Ph_2N_3Rh(H)_2]_2C_8H_{14}$ is 20:2.3:11.1 compared to the calculated ratio of 20:2:12.

$[(p\text{-}FC_6H_4)_2N_3Rh]_3C_8H_{12}$. A pressure bottle containing $(p\text{-}FC_6H_4)_2N_3RhC_8H_{12}$ (4.0 g, 9 mmol) and toluene (65 ml) was pressured with hydrogen (40 psig) and stirred 16 hr. The pressure dropped below atmospheric. The bottle was repressured and stirred another 6 hr. It was then vented; the contents were filtered and

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(14) P. S. Hallman, D. F. Evans, J. A. Osborn, and G. Wilkinson, *Chem. Commun.*, 305 (1968); R. A. Schunn and E. R. Wonchoba, *Inorg. Syn.*, **13**, 131 (1972).

evaporated, leaving a crystalline residue which was recrystallized from toluene and dried at 60°. The ^1H spectrum in toluene-d_8 included a hydride resonance identical with that of $[(C_6H_5)_2N_3Rh]_3$-C_8H_{12} while the ^{19}F spectrum (phenyl decoupled) of a fresh methylene chloride solution consisted of a temperature-independent singlet at −118.8 ppm (from F-11). On standing, additional resonances appeared at −118.4, −117.3, and −116.4 ppm. The analytical sample was again recrystallized from toluene and dried at 60° for 16 hr *in vacuo* (yield 0.71 g, 21%). *Anal.* Calcd for $C_{44}H_{42}F_6N_9Rh_3$: C, 47.20; H, 3.78; F, 10.18; N, 11.26; mol wt 1120. Found: C, 48.02; H, 3.25; F, 9.82; N, 11.33; mol wt 1190 (freezing point in benzene).

The observed aromatic:vinylic:methylene:hydridic proton nmr ratio was 25:3.3:8.7:5.5 compared with the calculated ratio of 24:4:8:6.

Registry No. I, 36126-19-9; I-F, 36126-20-2; II, 36118-98-6; II-F, 36118-99-7; III, 34840-63-6; IV, 36126-21-3; IV-F, 36126-22-4; V, 36118-96-4; V-F, 36118-97-5; VI, 36059-83-3; VI-F, 36059-84-4; VII, 36118-91-9; VIII, 36126-13-3; VIII-F, 36126-14-4; IX, 36126-15-5; X, 36126-16-6; XI, 36126-17-7; XI-F, 36085-75-3; XII, 12717-64-5; XII-F, 12717-61-2; XIII, 12717-59-8; $[(Ph_3P)_2RhN_3Ph_2]_2$, 12717-67-8; $Ph_2N_3Rh(C_8H_{12})NH_3$, 36118-95-3; $[Ni(N_3Ph_2)_2]_2$, 36126-18-8.

Contribution No. 2119 from the Department of Chemistry,
Indiana University, Bloomington, Indiana 47401

Transition Metal and Carborane Derivatives Obtained from Octadecaborane(22)

RAYMOND L. SNEATH[1] and LEE J. TODD*

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Reaction of *n*- or *i*-$B_{18}H_{20}^{2-}$ with a variety of phosphine- and carbonyl-substituted complexes of cobalt, rhodium, nickel, palladium, and platinum produced new metal-borane complexes of the general type $(B_{18}H_{20})M(\text{ligand})_n$. Cyclohexyl isocyanide reacts with *i*-$B_{18}H_{22}$ to form the carborane $B_{18}H_{20}CNH_2C_6H_{11}$. A nonpolar complex $B_{18}H_{20}(py)_2$ has been obtained by the reaction of pyridine with *n*-$B_{18}H_{22}$.

Introduction

Multigram quantities of a mixture of two isomeric $B_{18}H_{22}$ molecules can be conveniently prepared from $B_{10}H_{14}$ by the method of Pitochelli and Hawthorne.[2] Decaborane-14 is converted to $B_{10}H_{10}^{2-}$ which is oxidatively coupled with ferric chloride to form $B_{20}H_{18}^{2-}$. Controlled decomposition of the hydronium salt of $B_{20}H_{18}^{2-}$ yields the mixture of $B_{18}H_{22}$ isomers. The two isomers are separated by the column chromatographic procedure of Plesek and coworkers.[3] The structures of the two isomers have been determined by X-ray studies.[4,5] The $B_{18}H_{22}$ isomers are structurally related to decaborane and can be viewed as two decaborane molecules which are condensed together so that each half shares in common atoms B(6) and B(7) in the decaborane numbering system. These condensed-cage type boron hydrides are of particular interest because of the unique bonding which must be present at the juncture of the cage fragments. Employing reactions which had been successful earlier in decaborane(14) chemistry, we have been able to insert both metal and nonmetal elements into the B_{18} framework. The syntheses and characterizations of these new derivatives are the subject of this paper.

Experimental Section

Apparatus and Materials. The proton nmr spectra were obtained on a Varian HA-100 or HR-220 spectrometer. All boron (^{11}B) nmr spectra were obtained at 70.6 MHz with a Varian HR-220 spectrometer and were externally referenced to $BF_3 \cdot (C_2H_5)_2O$. Boron spectral integrals were obtained with a Lasico plainimeter.

The infrared spectra for which no solvent is indicated were measured as KBr disks. Infrared spectra were obtained with a Perkin-Elmer 621 or 137 instrument. The absorptions are reported as strong (s), medium (m), or weak (w). Spectra in the visible or ultraviolet range were obtained on a Cary 14 instrument. Mass spectra were obtained on an Atlas CH-7 or AEI MS-9 instrument. Molecular weights were obtained in $CHCl_3$ with a Mechrolab 301-A osmometer.

The $B_{18}H_{22}$ isomers and their salts were made by the method of Hawthorne[2] with the exception that their separation was accomplished by column chromatography using the method of Plesek.[3] $(PPh_3)_2NiCl_2$,[6] *trans*-$(PPh_3)_2Rh(CO)Cl$,[7] and $(Ph_2PCH_2CH_2PPh_2)MCl_2$ (where M = Ni,[8] Pd,[9] or Pt[10]) were prepared by published methods. $Co_2(CO)_8$ was purchased from Strem Chemicals. Elemental analyses were performed either at the University of Illinois Microanalytical Laboratory or by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

***n*-$B_{18}H_{20}Ni[P(C_6H_5)_3]_2$.** To a stirred slurry of 0.1 g of sodium hydride in 10 ml of dry tetrahydrofuran (THF) was added in small portions 0.2 g (0.92 mmol) of *n*-$B_{18}H_{22}$. Gas evolution was noted and the solution turned bright yellow. The solution was stirred at room temperature for 3 hr and Schlenk filtered into a 25-ml dropping funnel. The solution of $Na_2[n\text{-}B_{18}H_{20}]$ was then added dropwise to a stirred THF solution of 0.6 g (0.92 mmol) of $(Ph_3P)_2NiCl_2$. After all of the $Na_2[n\text{-}B_{18}H_{20}]$ had been added, the solution was stirred at reflux for 12 hr. The solvent was removed under vacuum after adding a small amount of silica gel to the mixture. The products were chromatographed on a silica gel column. Benzene eluted a red fraction. The crude product was crystallized from methylene chloride–hexane to give 0.214 g (27% yield) of *n*-$B_{18}H_{20}Ni(PPh_3)_2$.

The infrared spectrum of the complex contained absorption maxima at 3050 (w), 2416 (w), 1541 (s), 1483 (m), 1439 (s), 1190 (w), 1158 (w), 1093 (s), 1010 (m), 997 (m), 920 (w), 737 (m), 685 (s), 518 (s), 501 (m) cm^{-1}. The proton nmr spectrum of this complex in $CDCl_3$ gave a broad, poorly resolved resonance centered at τ 2.52. The elemental analyses of this compound and the other new compounds reported in this paper are given

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