

14871-47-7; RhCOCl(PPh₂Et)₂, 14875-00-4; RhCOBr(PPh₂Et)₂, 15134-27-7; RhCOCl(PPhEt₂)₂, 29553-46-6; RhCOBr(PPhEt₂)₂, 57636-59-6; RhCOCl(PPh₂Me)₂, 52611-29-7; RhCOCl(P(*m*-CH₃C₆H₄)₃)₂, 24554-72-1; RhCOCl(P(OPh)₃)₂, 25780-71-6; RhCOCl(P(OMe)₃)₂, 57587-14-1; IrCOBr(PPh₃)₂, 14970-06-0; IrCOCl(PPhEt₂)₂, 27488-97-7; IrCOCl(P(OPh)₃)₂, 15682-63-0; (P(OPh)₃)₂RhCl₂Rh(COD), 31781-80-3; Rh(CO)₂Cl(PPh₃)₃, 35679-01-7; RhCl(COD)(PPh₃)₃, 31781-57-4; Rh₂Cl₂(P(OMe)₃)₄, 49634-27-7; RhCOCl(PPh₃)(AsPh₃), 34347-94-9; RhCOCl(PPhEt₂)(Sb(*o*-CH₃C₆H₄)₃), 57587-15-2; RhCOCl(PPh₂Me)(PPh₃)₃, 39194-72-4; RhCOCl(PPh₂Me)(P(*m*-CH₃C₆H₄)₃), 57587-16-3; RhCOCl(PPh₂Me)(PPh₂Et), 57587-17-4; RhCOCl(PPh₂Me)(PPhEt₂), 57587-18-5; RhCOCl(PPh₂Me)(PEt₃), 57587-19-6; RhCOCl(PPhEt₂)(P(OPh)₃), 57587-20-9; IrCOCl(PPhEt₂)(P(OPh)₃), 57587-21-0; ³¹P, 7723-14-0.

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Contribution from C.N.R.-Centro di Studio sulla Stabilità e Reattività dei Composti di Coordinazione and Istituto di Chimica Analitica, University of Padova, Padua, Italy

1,2- and 1,7-Dicarba-closo-dodecaborane(12)-Iridium(I)

Complexes Formed through Metal-Carbon σ Bonds: Synthesis and Characterization.

Unusual Stereochemistry of the Oxidative Addition Reaction of Hydrogen

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A series of new stable iridium(I) complexes of the type *trans*-[(C₆H₅)₃P]₂Ir(CO)(σ -carb), where carb is 2-R-1,2-B₁₀C₂H₁₀⁻ (R = H, CH₃) and 7-R'-1,7-B₁₀C₂H₁₀⁻ (R' = H, CH₃, C₆H₅), has been prepared. Their infrared spectra are discussed. An analogous carborane complex containing CH₃(C₆H₅)₂P has also been prepared for NMR structural purposes. These complexes are isoelectronic and isostructural with the Vaska's complex but differ from this in two principal aspects: (a) the reaction with hydrogen is irreversible; (b) it occurs yielding three different isomers of cis addition as a result of solvent dependence of the hydrogen uptake. One of these isomers is not stable in solution and isomerizes, the type of the reaction product depending on the solvent used. The stereochemistry of the octahedral dihydrido derivatives obtained has been assigned by a combination of ir and ¹H NMR spectroscopy. Evidence supporting the kinetic control of the hydrogen addition is also reported.

Introduction

In the course of our research on the synthesis, characterization, and reactions of transition metal complexes containing 1,2- and 1,7-dicarba-closo-dodecaborane(12) formed through metal-carbon σ bonds,¹⁻⁶ we have prepared a series of stable uncharged iridium(I)-carborane complexes of general formula *trans*-[(C₆H₅)₃P]₂Ir(CO)(σ -carb), where carb is 2-R-1,2-B₁₀C₂H₁₀⁻ (R = H, CH₃) and 7-R'-1,7-B₁₀C₂H₁₀⁻ (R' = H, CH₃, C₆H₅).

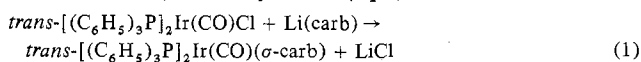
In spite of the remarkable interest concerning the properties and reactivities of various halogen and phosphine analogs of the Vaska complex, *trans*-[(C₆H₅)₃P]₂Ir(CO)Cl, only very few stable organometallic derivatives of these iridium(I) complexes have been reported.⁷⁻⁹

We wish to report here the preparation and characterization of some neutral iridium(I)-carborane complexes containing stable metal-carbon σ bonds. The reactions of these complexes

with molecular hydrogen are also reported together with a study of their stereochemical course.

Results and Discussion

Preparation and Characterization of the Iridium(I)-Carborane Complexes. Compounds of general formula *trans*-[(C₆H₅)₃P]₂Ir(CO)(σ -carb), carb = B₁₀C₂H₁₀R⁻, were obtained by treating a benzene suspension of *trans*-[(C₆H₅)₃P]₂Ir(CO)Cl with an excess of 1-Li-2-R-1,2-B₁₀C₂H₁₀ (R = H, CH₃) or 1-Li-7-R'-1,7-B₁₀C₂H₁₀ (R' = H, CH₃, C₆H₅) in diethyl ether (eq 1). In a similar manner



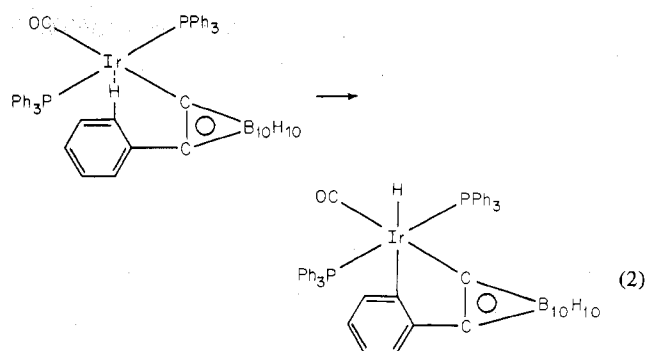
the complex *trans*-[(C₆H₅)₂CH₃P]₂Ir(CO)(σ -carb), where carb = 7-C₆H₅-1,7-B₁₀C₂H₁₀⁻, was also prepared. Table I lists the complexes obtained with pertinent analytical and ir (ν CO) data. Complexes I-VI (Table I) are stable under inert

atmosphere both in solution and in the solid state, are diamagnetic, and behave as nonelectrolytes at 25° in CH₂Cl₂ solution. The poor solubility of these complexes at low temperatures prevented measurement of their molecular weights by the cryoscopic method, whereas the high reactivity toward oxygen made unsuitable the osmometric method.

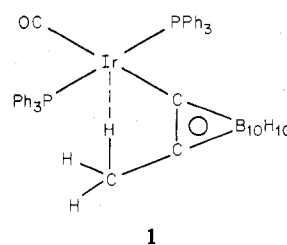
The ir spectra of I-VI, exhibit, in addition to the absorption bands due to the phosphine ligands, the strong absorption bands in the range 2540-2620 cm⁻¹ which are attributed to the B-H stretching of the dicarba-*closo*-dodecaborane(12) ligands and the strong bands due to ν_{CO} (Table I). The ν_{CO} frequencies found suggest a trans configuration for the complexes I-VI. In fact, bearing in mind that the electron-withdrawing ability of the carborane is comparable to that of the chloride ligand,¹⁰ the ν_{CO} frequencies shown are consistent with the expectation of a replacement of Cl⁻ by B₁₀C₂H₁₀R⁻ trans to CO in the complex *trans*-[(C₆H₅)₃P]₂Ir(CO)Cl (ν_{CO} 1967 cm⁻¹, CHCl₃¹¹), except for complex III (see below). The relative positions of the phosphine ligands have been investigated by ¹H NMR spectroscopy in connection with complex VI which contains the diphenylmethylphosphine ligands. The ¹H NMR spectrum of this complex shows a well-defined 1:2:1 triplet resonance at τ 7.74 [J(P-H) (apparent) = 3.0 Hz] of total relative intensity 2 due to the CH₃P protons, which is in agreement with two phosphines in mutually trans positions.¹²

It is to be noted that remarkable differences between the properties of the complexes containing as ligands the unsubstituted 1,2- or 1,7-carboranes and C(7)-substituted derivatives of 1,7-carborane and those of the complexes containing the C(2)-substituted derivatives of 1,2-carborane are observed. In the latter case the steric effects due to the presence of a substituent on the bulky carborane cage in the "ortho" position plays an important role. Thus, a peculiarity was encountered by treating *trans*-[(C₆H₅)₃P]₂Ir(CO)Cl with 1-Li-2-C₆H₅-1,2-B₁₀C₂H₁₀ in excess. The final product of this reaction is complex VII whose analytical and spectroscopic data are consistent with a hydridocarborane derivative of iridium(III). The ir spectrum (Nujol mull) exhibits, in addition to the absorptions of the carborane (ν_{BH} 2540-2620 cm⁻¹) and to those of the phosphine ligands, a strong band at 2010 cm⁻¹ assigned to ν_{CO} and two strong-medium absorptions at 2100 and 810 cm⁻¹ attributed to ν_{IrH} and δ_{IrH} , respectively. Furthermore, a strong band centered at 728 cm⁻¹ is observed which is in the typical range of the C-H out-of-plane deformation for ortho-disubstituted aromatics.¹³ The low solubility of complex VII in most of the solvents prevented any adequate ¹H NMR measurements. Actually, the first product of the reaction under discussion is an orange compound which is likely a carborane-iridium(I) complex, analogous to I-VI, formed through eq 1. This complex in the course of purification or on standing yields the white iridium(III) derivative, VII, which ought to form through an intramolecular oxidative addition reaction involving one ortho C-H bond of the C(2)-carborane ligand phenyl substituent, as shown in eq 2.

Steric requirements of the "ortho"-substituted carborane ligand may be responsible for this internal metalation, by forcing the iridium atom and the phenyl group of the carborane close together above the molecular plane^{14,15} as previously suggested in order to explain an identical intramolecular reaction observed in the formation of a similar hydridocarborane-rhodium(III) complex.⁵ Steric effects due to the C(2)-methyl-substituted carborane ligand may also explain the anomalously low ν_{CO} value (1950 cm⁻¹) found in the case of complex III. This complex, unlike the other iridium(I)-carborane complexes, is not soluble in most of the organic solvents and exhibits an exceptionally high reactivity toward



hydrogen oxidative addition also in the solid state (see below). We think that these peculiar aspects of complex III could be likely due (other than to a great molecular distortion induced by the substituted 1,2-carborane ligand) to a direct interaction between the C(2)-carborane methyl group and the iridium atom as shown in 1.



1

If this interaction was effective, an electron donation from the CH₃ group would take place and hence the nucleophilic power of the metal atom would be increased and it might also justify the exceptionally low ν_{CO} frequency exhibited by III. Structural information in this connection could be obtained by proton NMR spectroscopy of the corresponding 1-[(C₆H₅)₂CH₃P]₂Ir(CO)]-2-CH₃-1,2-(σ -B₁₀C₂H₁₀) complex (ν_{CO} 1954 cm⁻¹, Nujol). However, the preparation of such a complex leads to an unpurifiable compound whose low solubility in most organic solvents did not allow us to obtain an adequate NMR spectrum.

Reaction of Iridium(I)-Carborane Complexes with Molecular Hydrogen. The complexes *trans*-(R₂R'¹P)₂Ir(CO)-(σ -carb) (R = C₆H₅; R' = C₆H₅, CH₃) react rapidly with molecular hydrogen or deuterium giving dihydrides or di-deuterides of general formula (R₂R'¹P)₂IrH₂(or D₂)(CO)-(σ -carb). These complexes are colorless crystalline compounds, nonelectrolytes in solution, and very stable complexes with respect to thermal loss of either carborane or molecular hydrogen, but they are light sensitive. The stereochemical course of the oxidative addition reactions of hydrogen to carborane-iridium(I) complexes appears to be solvent dependent and three different isomeric adducts can be identified. Conversely, it is a well-known fact that the addition of hydrogen to related planar iridium(I) complexes is always stereospecifically cis and is unaffected by the nature of the solvent, a single isomer in which the phosphine ligands remain trans (configuration B, Figure 1) being formed.^{11,16,17}

Infrared and ¹H NMR data of the dihydridocarborane-iridium(III) isomers discussed in this report are listed in Table II.

Complex III, for which no information could be obtained with regard to the reaction with H₂ in solution owing to its insolubility, is very reactive toward hydrogen in the solid state. Thus, the reaction is complete in a few seconds at room temperature under 1 atm of hydrogen, yielding a single dihydridocarborane-iridium(III) isomer, X, which is soluble in the common organic solvents where it is indefinitely stable.

The ¹H (hydride) NMR spectrum of X is consistent with configuration C (Figure 1). In fact it shows two doublets of

Table I. σ -Bonded Iridium-Carborane Complexes

No.	Compd ^a	Color	Mp, °C	Yield, %	ν_{CO} , cm ⁻¹		
					Nujol	CHCl ₃	
I	1-[(Ph ₃ P) ₂ Ir(CO)]- 2-H-1,2-(σ -B ₁₀ C ₂ H ₁₀)	Yellow	183-184	75	Calcd: C, 52.75; H, 4.65 Found: C, 52.66; H, 4.63	1983 s	1977 s
II	1-[(Ph ₃ P) ₂ Ir(CO)]- 7-H-1,7-(σ -B ₁₀ C ₂ H ₁₀)	Yellow	173	70	Calcd: C, 52.75; H, 4.65 Found: C, 52.01; H, 4.65	1972 s	1968 s
III	1-[(Ph ₃ P) ₂ Ir(CO)]- 2-CH ₃ -1,2-(σ -B ₁₀ C ₂ H ₁₀)	Orange	183-184	90	Calcd: C, 53.25; H, 4.80 Found: C, 53.62; H, 4.30	1950 s	1953 s
IV	1-[(Ph ₃ P) ₂ Ir(CO)]- 7-CH ₃ -1,7-(σ -B ₁₀ C ₂ H ₁₀)	Yellow-orange	185-186	80	Calcd: C, 53.26; H, 4.80 Found: C, 53.03; H, 4.71	1970 s	1968 s
V	1-[(Ph ₃ P) ₂ Ir(CO)]- 7-C ₆ H ₅ -1,7-(σ -B ₁₀ C ₂ H ₁₀)	Orange	132-133	85	Calcd: C, 56.06; H, 4.70 Found: C, 56.30; H, 4.89	1970 s	1968 s
VI	1-[(Ph ₃ P) ₂ Ir(CO)]- 7-C ₆ H ₅ -1,7-(σ -B ₁₀ C ₂ H ₁₀)	Yellow-orange	187-189	85	Calcd: C, 50.05; H, 4.92 Found: C, 50.14; H, 4.98	1973 s	1975 s
VII	1-[(Ph ₃ P) ₂ Ir(CO)]-2-C ₆ H ₄ - 1,2-(σ -B ₁₀ C ₂ H ₁₀) ^{c,d}	White	193-195	75	Calcd: C, 56.06; H, 4.70 Found: C, 55.20; H, 4.64	2010 s	

^a Ph₃P = (C₆H₅)₃P; Ph₂MeP = (C₆H₅)₂CH₃P. ^b All compounds melt with decomposition in a capillary tube sealed under vacuum. ^c Molecular weight: calcd, 964; found, 930 (1,2-Cl₂C₂H₄ solution). ^d Ir bands (cm⁻¹) also at 2100 (m) [ν_{IrH}] and 810 (m) [δ_{IrH}] in Nujol.

Table II. Proton NMR and Ir Spectral Data on the Dihydrodicarbonyl-Iridium(III) Complexes, L₂IrH₂(CO)(σ -carb)

No.	carb	L	Confign	ν_{CO} , ^a cm ⁻¹	ν_{IrH} , ^a cm ⁻¹	Hydride resonances ^b			Other resonances ^b		
						τ , ppm	Mult ^c	J_{PH} , Hz	J_{HH} , Hz	τ , ppm	Assignment
VIII	2-H-1,2-B ₁₀ C ₂ H ₁₀	(C ₆ H ₅) ₃ P	A	2025 s	2162 s, 2144 m	19.97	cm		7.04, singlet	7.04, singlet	Carborane CH proton
IX	7-H-1,7-B ₁₀ C ₂ H ₁₀	(C ₆ H ₅) ₃ P	A	1998 s	2170 m, 2096 s	25.08	dt	21.0	5.2	7.79, singlet	Carborane CH proton
				1998 s	2177 m, 2122 s	18.47	dt	18.4	5.6	7.58, singlet	Carborane CH proton
X	2-CH ₃ -1,2-B ₁₀ C ₂ H ₁₀	(C ₆ H ₅) ₃ P	C	2000 s, 1991 sh (1995 s, CH ₂ Cl ₂)	2211 m, 2138 s	20.74	dd	22.0, 144.0	2.2	7.42, singlet	Carborane CH proton
				2000 s	2211 m, 2150 s	18.09	dd	22.3, 14.0	2.2	7.80, singlet	Carborane methyl protons
XI	7-CH ₃ -1,7-B ₁₀ C ₂ H ₁₀	(C ₆ H ₅) ₃ P	A	2021 s	2140 m, br (2150 m, br, DCE)	24.74	dt	21.7	5.6	8.78, singlet	Carborane methyl protons
				1984 s	2195 m, 2114 m, 2078 vw	18.50	dt	17.8	5.6	8.84, singlet	Carborane methyl protons
XII	7-C ₆ H ₅ -1,7-B ₁₀ C ₂ H ₁₀	(C ₆ H ₅) ₃ P	A	2001 s, 1994 s (1995 s, CH ₂ Cl ₂)	2204 m, 2142 s	20.84	dd	21.8, 144.3	2.8	8.64, singlet	Carborane methyl protons
				1991 s	2161 m, br 2210 m, 2149 m, 2064 vw	18.07	dd	22.4, 14.2	2.8	8.05, doublet ($J_{\text{PH}} = 6.9$ Hz)	Phosphine methyl protons
XIII	7-C ₆ H ₅ -1,7-B ₁₀ C ₂ H ₁₀	(C ₆ H ₅) ₂ CH ₃ P	A	1987 s	2196 w, 2138 s	20.77	dd	21.0, 144.0	2.4	7.63, triplet	Phosphine methyl protons
				1985 s	2156 m, 2112 s	19.52	cm	17.6	5.5	7.63, triplet ($J_{\text{PH}} = 3.3$ Hz ^d)	Phosphine methyl protons

^a Nujol mull. Key: s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad; DCE, in 1,2-dichloroethane solution. ^b Measured in CH₂Cl₂ at ca. 27° and 90 MHz. ^c τ values ± 0.01 ; J values ± 0.1 Hz. Chemical shifts measured relative to tetramethylsilane (τ 10.0 ppm). ^d Key: cm, complex multiplet; dt, doublet of triplets; dd, doublet of doublets. ^e Apparent coupling constant.

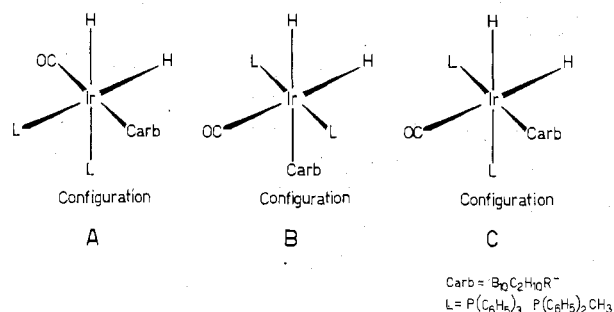
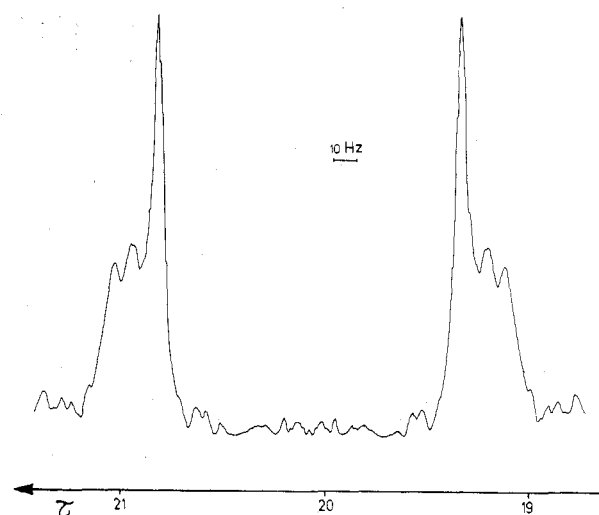


Figure 1.

doublets, both of total relative intensities 1, indicating that the hydride and the phosphine ligands are cis to each other (because of H-H coupling each peak is further split into two lines). The low-field resonance (τ 18.44) is assigned to hydrogen trans to CO,¹⁸ whereas the resonance at higher field (τ 21.48) together with the high J_{PH} value found is in agreement with a hydrogen trans to one phosphine ligand.¹⁸ Once the phosphines in this octahedral adduct were shown to be mutually cis, it was possible to confirm the remaining stereochemistry by use of infrared spectroscopy. Thus, the corresponding dideuterated complex was also prepared and an increase in ν_{CO} of 25 cm⁻¹ was observed in going from the dihydride to the dideuteride derivatives in agreement with the expectation of a CO trans to a H ligand,^{19,20} and it provides further support for the configuration C.

Complex V reacts with hydrogen in the solid state at room temperature although more slowly than complex III, the reaction being ended in about 1 hr. The dihydride so formed, XII, is a single stereoisomer, to which configuration A (Figure 1) has been assigned on the basis of the following considerations. The ¹H (hydride) NMR spectrum in CH₂Cl₂ of this adduct (Table II) is a complex centrosymmetrical multiplet centered at τ 19.52 (Figure 2). This hydride resonance pattern is characteristic of an AA'XX' spin system in which the two hydride ligands are mutually in cis position and are both trans to the phosphine ligands, thus leading to chemical but not magnetic equivalence. Moreover, the high ν_{CO} frequency exhibited by XII indicates that the CO group is trans to the carborane ligand (see above). Stereoisomers of type A can be obtained also by allowing complexes I, II, IV, and VI to react with hydrogen in the solid state. However, the reaction with these complexes is too slow to be a useful method for the preparation of isomers of type A. The dihydrides of this type are indefinitely stable in the solid state, whereas they isomerize quantitatively at room temperature in nonpolar solvents,²¹ such as CH₂Cl₂, 1,2-C₂H₄Cl₂, C₆H₆, etc., affording the stereoisomers of type B (Figure 1). The ¹H (hydride) NMR spectrum of the species B exhibits two 1:2:1 triplets indicating that the phosphine ligands are mutually trans (each peak of these triplets is further split into two lines by H-H coupling). The triplet at low field is due to the hydride trans to CO,¹⁸ that at high field ($\tau \sim 25$) being consequently attributable to the hydride trans to the carborane anionic ligand (Table II).

With the exception of the insoluble complex III, the carborane-iridium(I) complexes have been shown to be very reactive toward hydrogen in solution at room temperature. However, in these cases, the addition reaction exhibits a stereochemical course which changes with the solvent used. Thus, if the oxidative additions are carried out in polar solvents, such as CH₃CN, only adducts of configuration C are formed, whereas a mixture of stereoisomers is obtained working in nonpolar solvents, such as CH₂Cl₂ or C₂H₄Cl₂. Ir and ¹H (hydride) NMR spectroscopy of the latter reaction mixtures allowed us to detect only species A and B which appear to be

Figure 2. ¹H (hydride) NMR pattern of 1-[(Ph₃P)₂Ir(CO)H₂]-7-C₆H₅-1,7-(σ -B₁₀C₂H₁₀), configuration A (XII).

formed in all cases in the virtual molar ratio 6:4, which seems to be unaffected by the reaction temperature between -60 and +30°. However, species A is not stable in solution and slowly isomerizes quantitatively to B. By addition of methanol to the reaction mixture or by stripping the solvent, a mixture of the isomers A and B can be isolated in the solid state.

A more complete investigation on the H₂ uptake has been possible using complex IV, whose the reaction products exhibit a chemical shift of the CH₃ proton resonance of the 7-CH₃-1,7-B₁₀C₂H₁₀⁻ ligand which depends on the particular configuration of the complex (Table II). Thus, when the hydrogen addition is carried out in a nonpolar solvent, the ¹H NMR spectrum of the reaction product shows three different chemical shift values of the carborane CH₃ proton resonance, consistent with a mixture of isomers A (τ 8.78) and B (τ 8.84) and a small amount (2-5%) of isomer C (τ 8.64). The ¹H NMR spectrum run immediately after bubbling of hydrogen for 10 sec exhibits the carborane methyl proton resonances attributed to the growing species A, B, and C with relative intensities 6:4:0.2. The same relative intensities are found by recording the ¹H NMR spectrum after 5 min, when the starting complex is completely reacted.

These observations exclude that the formation of the stable species B and C is due merely to isomerization of A to B or A to C, thus showing that the reaction is kinetically controlled. Addition of CH₃CN ($\geq 2\%$ in volume) to a CH₂Cl₂ solution containing both stereoisomers A and B leads to quantitative isomerization of A to C, whereas isomer B appears to be stable.

Figure 3 shows the reaction sequence found in solution for the hydrogen addition to the carborane-iridium(I) complexes.

We think that steric crowding effects, resulting from the presence of the large carborane and phosphine ligands, can play an important part in determining the stereochemistry of the oxidative addition reactions in the cases of the carborane-iridium(I) complexes. In fact, these steric requirements are expected to induce a considerable distortion from the square-planar structure in the starting d⁸ complex.^{14,15} Consequently, the approach of H₂ above the molecular plane accompanied by simultaneous decrease in the P-Ir-P angle would give the adduct of configuration A in nonpolar solvents (eq 3), together with the stable species B.

The stereospecific course yielding the isomer of configuration C, observed when these hydrogen oxidative addition reactions are carried out in polar solvent, could be due to several unexplored reasons, such as the presence in solution of solvent-containing intermediates or simply as a thermodynamic solvent effect.

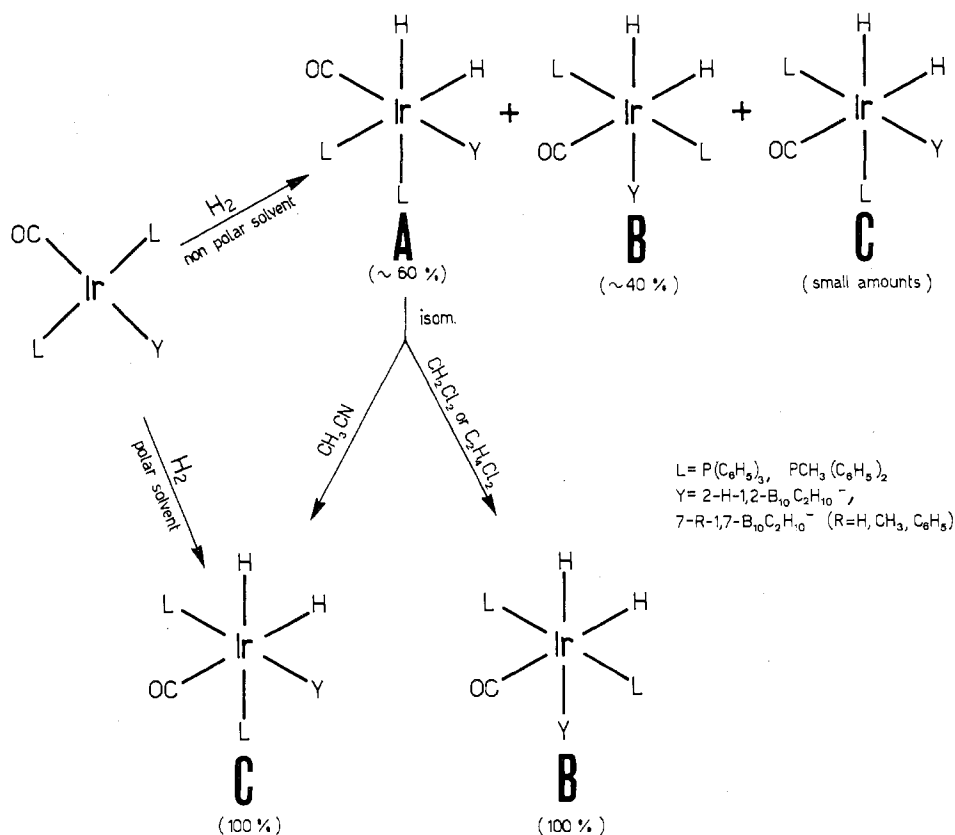
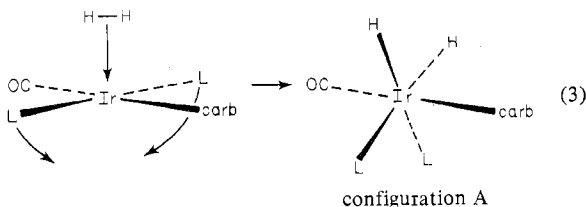


Figure 3.



Experimental Section

Reagent grade solvents were further purified by standard methods and were dried and degassed before use. The lithiocarboranes were prepared by treating the carboranes with lithium butyl as reported in the literature.²² *trans*-(PPh₃)₂Ir(CO)Cl and *trans*-(PPh₂Me)₂Ir(CO)Cl were prepared by literature methods.²³ All of the reactions involving iridium(I) complexes were carried out under argon atmosphere. ¹H 90-MHz NMR spectra were recorded with a Bruker HFX-90 spectrometer. Infrared spectra were obtained with a Perkin-Elmer Model 457 and calibrated against polystyrene film. Melting points were determined by a conventional hot-stage microscope and are uncorrected. Molecular weights were obtained by a Mechrolab Model 301 A osmometer.

1-[(Ph₃P)₂Ir(CO)]-2-H-1,2-(σ-B₁₀C₂H₁₀) (I). The solution obtained by treating 0.7 g (4.8 mmol) of 1-H-2-H-1,2-B₁₀C₂H₁₀ in 10 ml of diethyl ether with 3.25 ml of *n*-butyllithium (9.7% in hydrocarbons) was added to a suspension of 0.5 g (0.6 mmol) of *trans*-(Ph₃P)₂Ir(CO)Cl in 10 ml of C₆H₆ at room temperature. The resulting orange solution was stirred for 1 hr and then filtered. Addition of 40 ml of *n*-hexane to the resulted solution afforded yellow crystals which were washed with methanol and dried. The yield of pure product was 0.6 g (75%); mp 183–184° dec. ¹H NMR spectrum (CH₂Cl₂): broad singlet at τ 7.10 due to the CH carborane proton resonance.

1-[(Ph₃P)₂Ir(CO)]-7-H-1,7-(σ-B₁₀C₂H₁₀) (II). A suspension of 1-Li-7-H-1,7-B₁₀C₂H₁₀ (3.8 mmol) in 10 ml of diethyl ether was added to a suspension of 1 g (1.28 mmol) of *trans*-(Ph₃P)₂Ir(CO)Cl in 20 ml of benzene at room temperature. The mixture was stirred for 2 hr and the orange solution was then filtered. By addition of *n*-hexane a yellow precipitate was separated which was washed with methanol and further purified by recrystallization from CH₂Cl₂-CH₃OH. The yield of pure yellow crystals was 0.8 g (70%); mp 173° dec. ¹H NMR

spectrum (CH₂Cl₂): broad singlet at τ 7.64 due to the CH carborane proton resonance.

1-[(Ph₃P)₂Ir(CO)]-2-CH₃-1,2-(σ-B₁₀C₂H₁₀) (III). A solution of 3.4 mmol of 1-Li-2-CH₃-1,2-B₁₀C₂H₁₀ in 30 ml of diethyl ether was added to a solution of 1 g (1.28 mmol) of *trans*-(Ph₃P)₂Ir(CO)Cl in 50 ml of benzene at room temperature. After a few minutes a yellow-orange microcrystalline product was formed which was washed with *n*-hexane and methanol and dried in vacuo. The yield of orange microcrystals was 1.04 g (90%); mp 183–184° dec. The product appears to be insoluble in most of the organic solvents, but good analytical data were obtained without further purification.

1-[(Ph₃P)₂Ir(CO)]-7-CH₃-1,7-(σ-B₁₀C₂H₁₀) (IV). A solution of 7.5 mmol of 1-Li-7-CH₃-1,7-B₁₀C₂H₁₀ in 15 ml of diethyl ether was added to a suspension of 2 g (2.5 mmol) of *trans*-(Ph₃P)₂Ir(CO)Cl in 25 ml of benzene at room temperature and an orange solution was rapidly obtained. The LiCl formed was filtered off and then the addition of *n*-hexane caused separation of orange crystals which were separated by filtration, washed with methanol, and dried. The obtained product was purified by recrystallization from CH₂Cl₂-CH₃OH. The yield of pure yellow-orange crystals was 1.65 g (82%); mp 180–181° dec.

1-[(Ph₃P)₂Ir(CO)]-7-C₆H₅-1,7-(σ-B₁₀C₂H₁₀) (V). This complex was prepared as above by treatment of a solution of 1 g (1.28 mmol) of *trans*-(Ph₃P)₂Ir(CO)Cl in 30 ml of C₆H₆ with a solution of 3.4 mmol of 1-Li-7-C₆H₅-1,7-B₁₀C₂H₁₀ in 15 ml of ether. The crude product was further purified by recrystallization from benzene-*n*-hexane. The yield of pure product, orange crystals, was 1.0 g (85%); mp 132–133° dec.

1-[(Ph₂MeP)₂Ir(CO)]-7-C₆H₅-1,7-(σ-B₁₀C₂H₁₀) (VI). As complex V, this was prepared from a solution of 0.7 mmol of 1-Li-7-C₆H₅-1,7-B₁₀C₂H₁₀ in 10 ml of diethyl ether and a solution of 0.45 g (0.18 mmol) of *trans*-(Ph₂MeP)₂Ir(CO)Cl in 10 ml of benzene. The yield of pure orange crystals was 0.5 g (85%); mp 186–189° dec.

1-[(Ph₃P)₂IrH]-2-C₆H₅-1,2-(σ-B₁₀C₂H₁₀) (VII). Under argon, 3.4 mmol of a solution of 1-Li-2-C₆H₅-1,2-B₁₀C₂H₁₀ in 30 ml of anhydrous diethyl ether was slowly added to a stirred solution of 1 g (1.28 mmol) of *trans*-(Ph₃P)₂Ir(CO)Cl in 50 ml of anhydrous benzene at room temperature. The reaction mixture was stirred for 12 hr. The lithium chloride precipitate so formed was then separated by filtration in an argon atmosphere. Addition of *n*-hexane to the

resulting orange solution caused separation of a very air-sensitive orange product. Attempted purification of this crude product either by column chromatography (Al_2O_3 , benzene as eluent) or by recrystallization from $\text{CH}_2\text{Cl}_2\text{-CH}_3\text{OH}$ afforded pure white crystals, yield 75%, of VII, mp 193–195° dec.

Reaction of 1-[(Ph₃P)₂Ir(CO)]-2-H-1,2-($\sigma\text{-B}_{10}\text{C}_2\text{H}_{10}$), I, with H₂. Complex I (0.5 g) was dissolved in CH_2Cl_2 (10 ml) under argon and then hydrogen was bubbled through the solution at 25° for 3 min. The orange solution turned pale yellow. The ir and ¹H NMR spectra of this solution run within a very short time showed the presence of the dihydrido derivative in both configurations A and B. The solution was allowed to stand at room temperature for 24 hr and then addition of methanol precipitated a white solid, which was recrystallized from $\text{CH}_2\text{Cl}_2\text{-CH}_3\text{OH}$ to give white crystals of pure 1-[(Ph₃P)₂Ir(H₂)(CO)]-2-H-1,2-($\sigma\text{-B}_{10}\text{C}_2\text{H}_{10}$), configuration B (VIII), mp 170–171° dec. Anal. Calcd for C₃₉H₄₃B₁₀OP₂Ir: C, 52.63; H, 4.87. Found: C, 51.95; H, 4.80.

Reaction of 1-[(Ph₃P)₂Ir(CO)]-7-H-1,7-($\sigma\text{-B}_{10}\text{C}_2\text{H}_{10}$), II, with H₂. (a) The procedure was as described above, using 0.15 g of II in 1.5 ml of CH_2Cl_2 . The initially orange solution turned pale yellow within 15 min. A mixture of adducts of configurations A and B (IV) was formed. The solution was allowed to stand at 40° for 5 hr and then methanol was added and the precipitate was recrystallized from $\text{CH}_2\text{Cl}_2\text{-CH}_3\text{OH}$ to give white crystals of pure 1-[(Ph₃P)₂Ir(H₂)(CO)]-7-H-1,7-($\sigma\text{-B}_{10}\text{C}_2\text{H}_{10}$), configuration B, IX, mp 161–162° dec. Anal. Calcd for C₃₉H₄₃B₁₀OP₂Ir: C, 52.63; H, 4.87. Found: C, 52.20; H, 4.91.

(b) By treating complex II with hydrogen in CH_3CN solution as described above, a white precipitate was rapidly formed. This crude product was purified by recrystallization from $\text{CH}_2\text{Cl}_2\text{-CH}_3\text{OH}$ yielding white crystals of pure 1-[(Ph₃P)₂Ir(H₂)(CO)]-7-H-1,7-($\sigma\text{-B}_{10}\text{C}_2\text{H}_{10}$), configuration C (IX). Anal. Calcd for C₃₉H₄₃B₁₀OP₂Ir: C, 52.63; H, 4.87. Found: C, 52.60; H, 4.85.

Reaction of 1-[(Ph₃P)₂Ir(CO)]-2-CH₃-1,2-($\sigma\text{-B}_{10}\text{C}_2\text{H}_{10}$), III, with H₂. (a) Crystals of III were kept under hydrogen at 25° (1 atm) and the orange solid immediately turned white. The crude product was purified by recrystallization from $\text{CH}_2\text{Cl}_2\text{-CH}_3\text{OH}$ to give white crystals of pure 1-[(Ph₃P)₂Ir(H₂)(CO)]-2-CH₃-1,2-($\sigma\text{-B}_{10}\text{C}_2\text{H}_{10}$), configuration C (X), mp 161° dec. Anal. Calcd for C₄₀H₄₅B₁₀OP₂Ir: C, 53.14; H, 5.02. Found: C, 52.60; H, 5.07. The corresponding dideuteride was prepared similarly using deuterium. Ir bands (cm^{-1}) at 1583 (m) and 1520 (w) were due to ν_{IRD} and that at 2025 (s) was due to ν_{CO} (Nujol).

(b) By bubbling hydrogen through a CH_2Cl_2 suspension of III at room temperature, a colorless solid was rapidly formed which resulted in being a mixture of isomeric adducts having poor solubility and it was no further investigated. ν_{IR} maxima (cm^{-1}) are at 2247 (m), 2230 (m), 2130 (s), and 2115 (s) [ν_{IRH}] and at 1997 (s) and 1981 (s) [ν_{CO}] in Nujol.

Reaction of 1-[(Ph₃P)₂Ir(CO)]-7-CH₃-1,7-($\sigma\text{-B}_{10}\text{C}_2\text{H}_{10}$), IV, with H₂. (a) Crystals of IV were kept under hydrogen (1 atm) at room temperature for 12 hr. According to ir and NMR spectroscopy the white solid so formed appears to contain the dihydride adduct of configuration A (XI) together with unreacted complex IV. Attempts to isolate the pure isomer A by recrystallization were unsuccessful since isomerization to species B takes place in solution of CH_2Cl_2 .

(b) Complex IV (0.3 g) was dissolved in 1,2-dichloroethane (20 ml) under argon and hydrogen was bubbled through the solution at 25°. The initially orange solution turned colorless in the course of 3 min. Addition of ethanol caused a white precipitate which according to ir and ¹H NMR (in CH_2Cl_2) spectroscopy turned out to be a mixture of the dihydride adducts of configurations A, B, and C (60, 35, and 5%, respectively) (XI, Table II). The same mixture was obtained when the reaction was carried out in CH_2Cl_2 solution. This mixture of isomeric adducts was then dissolved in CH_2Cl_2 and the obtained solution was allowed to stand at room temperature for 24 hr. Addition of methanol to this solution and recrystallization of the resulting precipitate from $\text{CH}_2\text{Cl}_2\text{-CH}_3\text{OH}$ gave pure XI, configuration B, mp 153° dec. Anal. Calcd for C₄₀H₄₅B₁₀OP₂Ir: C, 53.14; H, 5.02. Found: C, 52.90; H, 4.98.

(c) The procedure was as described in (b), using as solvent CH_3CN in place of CH_2Cl_2 . The initially orange solution turned colorless in the course of 2 min and a white crystals solid began to precipitate. After 30 min this was filtered, washed with methanol, and recrystallized from $\text{CH}_2\text{Cl}_2\text{-CH}_3\text{OH}$ to give white crystals of pure 1-[(Ph₃P)₂Ir(H₂)(CO)]-7-CH₃-1,7-($\sigma\text{-B}_{10}\text{C}_2\text{H}_{10}$), configuration C (XI),

mp 163–164° dec. Anal. Calcd for C₄₀H₄₅B₁₀OP₂Ir: C, 53.14; H, 5.02. Found: C, 52.50; H, 5.04. The adduct of configuration C was also obtained using nitromethane or dimethylformamide as reaction solvent.

The corresponding dideuteride (mp 162–164° dec) was prepared similarly in CH_3CN solution using deuterium. Bands due to ν_{CO} were seen at 2020 (s) cm^{-1} in Nujol and at 2021 (s) cm^{-1} in CH_2Cl_2 .

Reaction of 1-[(Ph₃P)₂Ir(CO)]-7-C₆H₅-1,7-($\sigma\text{-B}_{10}\text{C}_2\text{H}_{10}$), V, with H₂. (a) Crystals of V were kept under hydrogen (1 atm) at room temperature. The initially orange product lightened in color and in the course of 20 min a pale yellow solid was obtained. According to spectroscopic evidence this turned out to be the dihydride of configuration A (XII) together with a small amount of the unreacted complex V. Isomerization of the species A occurs when purification by recrystallization was tried.

(b) The dihydrido derivative obtained as described above was dissolved in CH_2Cl_2 . After 1 day at room temperature a white product was precipitated with ethanol which was recrystallized from $\text{CH}_2\text{Cl}_2\text{-CH}_3\text{OH}$ to give white crystals of pure 1-[(Ph₃P)₂Ir(H₂)(CO)]-7-C₆H₅-1,7-($\sigma\text{-B}_{10}\text{C}_2\text{H}_{10}$), configuration B (XII), mp 142–143° dec. Anal. Calcd for C₄₅H₄₇B₁₀OP₂Ir: C, 55.95; H, 4.90. Found: C, 55.62; H, 4.81.

(c) The dihydrido derivative prepared as described in (a) was dissolved in CH_2Cl_2 containing CH_3CN (10% by volume). The solution was kept for 1 day at room temperature. Thus, ethanol was added and the precipitate recrystallized from $\text{CH}_2\text{Cl}_2\text{-CH}_3\text{OH}$ to give white crystals of 1-[(Ph₃P)₂Ir(H₂)(CO)]-7-C₆H₅-1,7-($\sigma\text{-B}_{10}\text{C}_2\text{H}_{10}$), configuration C, mp 140° dec. Anal. Calcd for C₄₅H₄₇B₁₀OP₂Ir: C, 55.95; H, 4.90. Found: C, 55.80; H, 4.93.

Reaction of 1-[(Ph₂MeP)₂Ir(CO)]-7-C₆H₅-1,7-($\sigma\text{-B}_{10}\text{C}_2\text{H}_{10}$), VI, with H₂. Complex VI (0.5 g) was dissolved in CH_2Cl_2 (40 ml) under argon and then hydrogen was passed at 25°. The orange solution rapidly turned colorless. Ir and ¹H NMR spectra run after few minutes revealed the presence of both adducts of configurations A and B (XIII). By allowing this solution to stand at room temperature for 2 days, complete isomerization to isomer B was observed. Ethanol was then added and the precipitate recrystallized from $\text{CH}_2\text{Cl}_2\text{-CH}_3\text{OH}$ gave white crystals of pure 1-[(Ph₂MeP)Ir(H₂)(CO)]-7-C₆H₅-1,7-($\sigma\text{-B}_{10}\text{C}_2\text{H}_{10}$), configuration B (XIII), mp 169–170° dec. Anal. Calcd for C₃₅H₄₃B₁₀OP₂Ir: C, 49.92; H, 5.15. Found: C, 49.86; H, 5.24.

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Registry No. I, 57527-15-8; II, 57527-14-7; III, 57527-13-6; IV, 57527-12-5; V, 57527-11-4; VI, 57527-10-3; VII, 57527-09-0; VIII-A, 57550-03-5; VIII-B, 57527-08-9; IX-A, 57550-02-4; IX-B, 57550-01-3; IX-C, 57527-07-8; X-C, 57527-06-7; XI-A, 57550-00-2; XI-B, 57549-99-2; XI-C, 57527-05-6; XII-A, 57549-98-1; XII-B, 57549-97-0; XII-C, 57527-04-5; XIII-A, 57549-96-9; XIII-B, 57527-03-4; 1-H-2-H-1,2-B₁₀C₂H₁₀, 16872-09-6; 1-Li-7-H-1,7-B₁₀C₂H₁₀, 32630-06-1; 1-Li-2-CH₃-1,2-B₁₀C₂H₁₀, 32630-05-0; 1-Li-7-CH₃-1,7-B₁₀C₂H₁₀, 32630-07-2; 1-Li-7-C₆H₅-1,7-B₁₀C₂H₁₀, 42012-25-9; 1-Li-2-C₆H₅-1,2-B₁₀C₂H₁₀, 41655-52-1; *trans*-(Ph₃P)₂Ir(CO)Cl, 15318-31-7; *trans*-(Ph₂MeP)₂Ir(CO)Cl, 15318-32-8; H₂, 1333-74-0.

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Aromatic Nitroso Compounds as π Acids in the Zerovalent Nickel Triad Metal Complexes and the Metal-Assisted Atom-Transfer Reactions with Donor Reagents

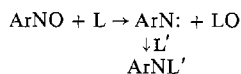
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Mono- and trinuclear arylnitroso complexes of the nickel triad, $M(\text{ArNO})(t\text{-BuNC})_2$ [$M = \text{Ni}$, $\text{Ar} = p\text{-XC}_6\text{H}_4$ ($X = \text{NMe}_2$, OMe , Me , H , Cl , Br), $3,4\text{-Cl}_2\text{C}_6\text{H}_3$; $M = \text{Pd}$, $\text{Ar} = p\text{-ClC}_6\text{H}_4$], $M(\text{PhNO})(\text{PPh}_3)_2$ ($M = \text{Ni}$, Pd , Pt), and $\text{Pd}_3(\text{PhNO})_3\text{L}_3$ [$\text{L} = \text{P}(t\text{-Bu})_3$, $\text{PPh}(t\text{-Bu})_2$], have been prepared. Ir data of the mono- and trinuclear compounds suggest a side-on η^2 coordination of the $\text{N}=\text{O}$ group which has been confirmed by an x-ray analysis on the latter compound. For $M(\text{ArNO})(t\text{-BuNC})_2$, the $\text{N}=\text{C}$ stretching frequencies (A' and A'' modes) correlate linearly with the Hammett σ constant (σ_p) of the para substituent. Consistently a linear correlation was found between the upfield shift ($\Delta\tau$) of meta protons and the cis stretch-stretch interaction $\Delta\nu(\text{N}=\text{C})$. The property of nitrosobenzenes as two-center π acids has been discussed on the basis of the spectral data. Facile $\text{N}-\text{O}$ bond cleavage of the coordinated PhNO leading to phenylnitrene and oxygen atom transfer was observed when $\text{Ni}(\text{PhNO})(t\text{-BuNC})_2$ was treated with electron-donating reagents, $t\text{-BuNC}$, PPh_3 , and PhNO . The reaction of PhNO with $t\text{-BuNC}$ to give $t\text{-BuNCO}$, $\text{PhN}=\text{N}(\text{O})\text{Ph}$, and $\text{PhN}=\text{C}=\text{N}(t\text{-Bu})$ can be carried out as a catalytic process. Metal-catalyzed atom-transfer reactions between the nitro compound and $t\text{-BuNC}$ were also described.

In most of the nitrosobenzene^{1,2} or substituted nitrosobenzene complexes^{3,4} so far prepared the ligand coordinates to a metal as a σ base through the N or O atom, although conclusive evidence for their structures is lacking. A recent x-ray study of *trans*- $\text{PdCl}_2(\text{PhNO})_2$ revealed η^1 coordination through the N atom.⁵ The $-\text{NO}$ group in the nitroso compound, isoelectronic (12 electrons) to dioxygen, should be able to act as a two-center π acid. There has been only one example, $\text{Fe}_2(\text{CO})_6(3\text{-Cl-2-CH}_3\text{C}_6\text{H}_3\text{NO})_2$,⁶ for which η^2 coordination has been established.⁷ We were interested in obtaining a series of mononuclear transition metal compounds having an η^2 -ligated nitroso compound for information on the nature of their bonding. In such an attempt we obtained a stable trinuclear compound $\text{Pd}_3(\text{PhNO})_3[\text{P}(t\text{-Bu})_3]_3$ and reported briefly the x-ray structure.⁸ In this paper we describe the preparation of mononuclear compounds of the type $M(\eta^2\text{-nitrosobenzene})\text{L}_2$ ($M = \text{Ni}$, Pd , Pt ; $\text{L} = t\text{-BuNC}$, PPh_3) and their spectroscopic data relevant to a discussion of the bonding to metal. The spectral properties suggestive of considerable perturbation of the NO bond upon coordination prompted us to study the reactivity of coordinated nitroso compounds. Nitrosobenzenes are considerably reactive. For example, the deoxygenation occurs readily with trivalent phosphorus compounds leading to nitrene reactions.⁹ This type of reaction was also observed with $\text{Fe}(\text{salen})$ ($\text{salen} = N,N'$ -ethylenebis(salicylaldiminato)).¹⁰ Some metal-assisted atom-transfer redox reactions were also reported without details.^{11,12}



From the reactivity studies, we were able to convert a stoichiometric atom-transfer reaction into a catalytic process.

Results and Discussion

Preparation, Properties, and Structure. The complex $\text{Ni}(t\text{-BuNC})_n$ ¹³ ($n = 2$ or 4) suspended in *n*-hexane was treated

with an equimolar amount of $p\text{-XC}_6\text{H}_4\text{NO}$ ($X = \text{Me}_2\text{N}$, MeO , Me , H , Cl , Br) or $3,4\text{-Cl}_2\text{C}_6\text{H}_3\text{NO}$ at room temperature to obtain quantitatively diamagnetic complexes $\text{Ni}(\text{ArNO})(t\text{-BuNC})_2$ as red microcrystals. The reaction with an excess of PhNO under nitrogen gave unexpectedly a nitrobenzene complex $\text{Ni}(\text{PhNO}_2)(t\text{-BuNC})_2$.¹² A similar reaction of " $\text{Pd}(t\text{-BuNC})_2$ "¹³ with $p\text{-ClC}_6\text{H}_4\text{NO}$ yields a diamagnetic orange complex $\text{Pd}(p\text{-ClC}_6\text{H}_4\text{NO})(t\text{-BuNC})_2$. Triphenylphosphine analogues $M(\text{PhNO})(\text{PPh}_3)_2$ ($M = \text{Ni}$, Pd , Pt) are prepared from $M(\text{CH}_2=\text{CH}_2)(\text{PPh}_3)_2$ ¹⁴⁻¹⁶ and PhNO in *n*-hexane. In contrast, a similar reaction of the two-coordinate phosphine complex PdL_2 ¹⁷ ($\text{L} = \text{P}(t\text{-Bu})_3$, $\text{PPh}(t\text{-Bu})_2$) affords a trinuclear complex $\text{Pd}_3(\text{PhNO})_3\text{L}_3$ ⁸ as red crystals with liberation of 1 mol of phosphine. The steric bulk of $\text{P}(t\text{-Bu})_3$ (cone angle¹⁸ $180 \pm 2^\circ$) and $\text{PPh}(t\text{-Bu})_2$ (cone angle¹⁹ $170 \pm 2^\circ$) apparently prevents the formation of $\text{Pd}(\text{PhNO})\text{L}_2$.

The isocyanide complexes $M(\text{ArNO})(t\text{-BuNC})_2$ are monomeric and readily soluble in benzene, ether, and acetone but insoluble in saturated hydrocarbons. The nickel isocyanide complexes are unstable in air and even in the solid state, while the palladium complex is stable in the solid state for a few hours. The triphenylphosphine complexes are less soluble in benzene and more stable toward air compared to the isocyanide analogues. The trinuclear complexes $\text{Pd}_3(\text{PhNO})_3\text{L}_3$ are soluble in *n*-hexane and stable in air in solution. The thermal stability of the nickel isocyanide complexes increases with increase of electron-accepting property of the para substituent of the nitroso compounds, as manifested qualitatively in their decomposition temperatures (Table I).

Assignment of the $\text{N}=\text{O}$ stretching of nitrosobenzenes appears not to have been settled yet. The absorption at ~ 1500 cm^{-1} has been assigned as $\nu(\text{N}=\text{O})$,²¹ while Nakamoto et al.²² assigned the absorption at $1340\text{--}1350$ cm^{-1} as $\nu(\text{N}=\text{O})$. The ir spectra of the coordinated nitrosobenzenes (Table II), lacking absorptions in these regions, show a new strong band in a region of $978\text{--}1040$ cm^{-1} . These bands were not observed in *trans*- $\text{PdCl}_2(\text{PhNO})_2$ ² where PhNO coordinates as a ni-