systems (see Table I).

The only differences through the series of potential five-coordinate complexes were the small but real changes in the $\perp$ region. The Q-band spectra show the expected rhombic symmetry of the $Cu(TAAB)[X(CH_2CH_2O)_2]$ and $Cu(TAAB)(OCH_3)_2$ compounds. The g_{xx} and g_{yy} values are easily calculated from the Q-band spectra. For a planar molecule with axial symmetry, such as $Cu(TAAB)^{2+}$, g_{xx} was found to be equal to g_{yy}, as expected. A small spectral difference observable only in the ESR spectra (not optical or IR) at 35 GHz indicates only a small electronic difference between the three compounds. At this point, the question of axial coordination must be addressed. It is possible to imagine a *trans-spanning* ligand containing a heteroatom but not donating electron density to the copper atom. Bailar and co-workers[13] prepared *trans-spanning* bidentate ligands coordinated to Pt(II) some time ago (even though they were only recently reported). It is our contention, from the data presented here, that no fifth, axial coordination from sulfur, nitrogen, or oxygen exists. The small electronic changes observed from the ESR data are best explained by a weak interaction of the axial donor with copper(II) but are not strong enough to be classified as a normal bond.

We have made to date several unsuccessful attempts to obtain the complexes in a crystalline form suitable for a single-crystal X-ray structural study.

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Contribution from the Department of Chemistry,
University of Georgia, Athens, Georgia 30602

(Triphenylcyclopropenyl)nickel Derivatives as Catalysts for the Isomerization of Quadricyclane to Norbornadiene

R. B. KING* and S. IKAI

Infrared spectroscopy indicates that the (triphenylcyclopropenyl)nickel complex $(C_6H_5)_3C_3Ni(CO)Cl$ readily loses its CO ligand in solution at room temperature but reacts with CO at room temperature and atmospheric pressure to form successively $(C_6H_5)_3C_3Ni(CO)_2Cl$ and $Ni(CO)_4$. Reactions of $(C_6H_5)_3C_3Ni(CO)Cl$ with various ligands in solution at room temperature rapidly give complexes with a L:Ni ratio of 2:1 of the type $(C_6H_5)_3C_3NiL_2Cl$ (L = tetrahydrofuran, 2,2'-bipyridyl, $(C_6H_5)_2PCH_3$, $(C_6H_5)_2PCl$, $C_6H_5PCl_2$, and $P(OR)_3$ (R = phenyl, isopropyl, and methyl)). The ligand $(C_6H_5)_2PCH_3$ also gives an isolable 1:1 L–Ni complex of the stoichiometry $(C_6H_5)_3C_3Ni[P(C_6H_5)_2CH_3]Cl$. The complex $(C_6H_5)_3C_3Ni(CO)Cl$ is an active catalyst for the isomerization of quadricyclane to norbornadiene under conditions where it is converted to a carbonyl-free complex. Addition of the ligands L to $(C_6H_5)_3C_3Ni(CO)Cl$ in L:Ni ratios from 1:1 to 3:1 gradually reduces the catalytic activity of these systems. The catalytic activities of the $(C_6H_5)_3C_3NiL_2Cl$ derivatives (L = trivalent phosphorus ligand) increase as the coordination chemical shift decreases in their phosphorus-31 NMR spectra.

Introduction

In connection with the development of a system for the chemical storage of solar energy based on the reversible valence isomerization of norbornadiene (I) to quadricyclane (II),[1-3] we have screened diverse transition-metal complexes for catalytic activity for the exothermic conversion of quadricyclane to norbornadiene. One of the relatively few derivatives found to exhibit high catalytic activity for this reaction was the (triphenylcyclopropenyl)nickel complex originally[4] formulated as the dimer $[(C_6H_5)_3C_3Ni(CO)Cl]_2$ but subsequently[5] reformulated as the monomer (III: X = Cl) by analogy with the corresponding tri-*tert*-butylcyclopropenyl derivative shown to be a monomer by solution molecular weight determinations.

Since (triphenylcyclopropenyl)nickel derivatives represented a new type of catalyst structure and since the chemistry of such

I   II

III
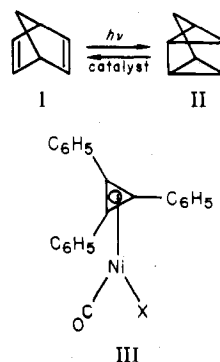
systems was only poorly known, we initiated a detailed study of the preparations and reactions of (triphenylcyclopropenyl)nickel derivatives as well as their use as catalysts for the

conversion of quadricyclane to norbornadiene. This work is described in this paper.

Experimental Section

Microanalyses were performed by Atlantic Microanalytical Laboratory, Atlanta, Ga. Proton NMR spectra were taken in $CDCl_3$ solutions and recorded at 60 MHz on a Varian T-60 spectrometer. Phosphorus-31 NMR spectra were taken in dichloromethane solutions and recorded at 40.3 MHz on a Jeolco PFT-100 spectrometer operating in the pulsed Fourier-transform mode with proton noise decoupling and a deuterium lock. Upfield chemical shifts relative to external 85% phosphoric acid are designated as positive. Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. Melting and decomposition points were taken in capillaries and are uncorrected.

All nickel complexes prepared in this study are very air and moisture sensitive in solution; solvents were therefore saturated with nitrogen and dried before use. Thus dichloromethane was dried over P_4O_{10} and distilled under nitrogen. Tetrahydrofuran was distilled under nitrogen over sodium benzophenone ketyl.

The trivalent phosphorus ligands $P(OCH_3)_3$, $P[OCH(CH_3)_2]_3$, $P(OC_6H_5)_3$, $(C_6H_5)_2PCl$, and $C_6H_5PCl_2$ were purchased from Aldrich Chemical Co., Milwaukee, Wis., and were distilled before use. The methyldiphenylphosphine, $(C_6H_5)_2PCH_3$, was prepared by the reaction of $(C_6H_5)_2PCl$ with CH_3MgI.[6] Other chemicals were purified by standard methods.

The (triphenylcyclopropenyl)nickel carbonyl halides $(C_6H_5)_3C_3Ni(CO)X$ (X = Cl and Br) were prepared from $Ni(CO)_4$ and the corresponding triphenylcyclopropenyl halides by use of the methods of Kettle and Gowling.[4] The $(C_6H_5)_3C_3Ni(CO)Cl$ was converted to $(C_6H_5)_3C_3Ni(NC_5H_5)_2Cl\cdot NC_5H_5$[7] and $(C_6H_5)_3C_3Ni\text{-}C_5H_5$[8] by the cited published methods.

Decomposition of $(C_6H_5)_3C_3Ni(CO)Cl$ in Dichloromethane. A solution of 0.2 g (0.514 mmol as monomer) of $(C_6H_5)_3C_3Ni(CO)Cl$ in 200 mL of dichloromethane was vigorously stirred at 30 °C for 30 min. The resulting dark red solution was concentrated at 25 °C (25 mm) to a total volume of 20 mL. The solution was filtered to separate a small amount of insoluble material. After addition of 5 mL of hexane, the solution was allowed to stand at -10 °C overnight to give 0.03 g of a dark brown solid, mp 183–190 °C dec, exhibiting no infrared $\nu(CO)$ frequencies and analyzing for $6(C_6H_5)_3C_3NiCl\cdot NiCl_2$. Anal. Calcd for $C_{126}H_{90}Ni_7Cl_8$: C, 65.8; H, 3.9; Cl, 12.4. Found: C, 65.2; H, 3.8; Cl, 12.2.

Preparation of $(C_6H_5)_3C_3NiL_2Cl$ Derivatives. (1) L = Tetrahydrofuran. A solution of 0.1 g (0.26 mmol) of $(C_6H_5)_3C_3Ni(CO)Cl$ in 200 mL of tetrahydrofuran was stirred vigorously at 30 °C until the solution became almost homogeneous. The solution was concentrated to 20 mL by evaporation at 25 °C (25 mm). A small amount of insoluble material was removed by filtration. Cooling the filtrate overnight at -10 °C gave 0.09 g (69% yield) of dark brown solid $(C_6H_5)_3C_3Ni(OC_4H_8)_2Cl$: mp 75 °C dec; proton NMR τ 2.42–3.20 (multiplet, 15 H, phenyl), τ 6.23 (broad singlet, 8 H, THF), and τ 8.10 (broad singlet, 8 H, THF). Anal. Calcd for $C_{29}H_{31}ClNiO_2$: C, 68.9; H, 6.2; Cl, 7.0. Found: C, 68.4; H, 6.2; Cl, 7.3. Additional product was isolated by evaporation of the filtrate.

(2) L_2 = 2,2'-Bipyridyl. A solution of 0.3 g (0.77 mmol) of $(C_6H_5)_3C_3Ni(CO)Cl$ in 30 mL of tetrahydrofuran was treated with 0.138 g (0.88 mmol) of 2,2'-bipyridyl at room temperature. After stirring of the solution for 5 min, the dark red solution was filtered. The filtrate was evaporated at 25 °C (25 mm) to a volume of 15 mL. The resulting dark red tetrahydrofuran solution containing some precipitated product was heated at 40 °C to dissolve the solids. Very fine dark red crystals were obtained by keeping the solution at -10 °C overnight to give 0.25 g (60% yield) of $(C_6H_5)_3C_3Ni(N_2C_{10}H_8)Cl$: mp 170 °C dec; proton NMR τ 1.1–1.3 (multiplet, 2 H, bipyridyl), τ 2.0–3.0 (multiplet, 21 H, bipyridyl and phenyl). Anal. Calcd for $C_{31}H_{23}ClN_2Ni$: C, 71.9; H, 4.5; N, 5.4. Found: C, 70.5; H, 4.4; N, 5.3. This product is stable in air for several weeks.

(3) L = $(C_6H_5)_2PCH_3$. A solution of 0.3 g (0.77 mmol) of $(C_6H_5)_3C_3Ni(CO)Cl$ in 10 mL of dichloromethane was treated with 0.34 g (1.7 mmol) of methyldiphenylphosphine at room temperature. This mixture was stirred for 5 min and then filtered. The filtrate was treated with 10 mL of *n*-hexane. Concentration at 25 °C (25 mm) followed by crystallization of the dark red precipitate from a mixture of benzene and dichloromethane gave 0.40 g (64% yield) of $(C_6H_5)_3C_3Ni[P(C_6H_5)_2CH_3]_2Cl$: mp 140 °C dec; proton NMR τ

2.3–3.2 (multiplet, 35 H, phenyl), τ 8.60 (broad singlet, 6 H, methyl). Anal. Calcd for $C_{47}H_{41}ClNiP_2$: C, 74.1; H, 5.4; Cl, 4.6. Found: C, 73.8; H, 5.4; Cl, 4.5. This product is stable in air for several weeks.

(4) L = $(C_6H_5)_2PCl$. A solution of 0.40 g (1.02 mmol) of $(C_6H_5)_3C_3Ni(CO)Cl$ in 10 mL of dichloromethane was treated with 0.49 g (2.24 mmol) of $(C_6H_5)_2PCl$ at room temperature. The orange solution was stirred for 5 min and then filtered. The filtrate was evaporated to dryness at 25 °C (25 mm). The residue was washed twice with 5 mL of cold benzene and then dissolved in 5 mL of benzene at 30 °C. Keeping this solution at -10 °C deposited 0.47 g (55% yield) of very fine orange solid $(C_6H_5)_3C_3Ni[P(C_6H_5)_2Cl]_2Cl$: mp 115 °C dec; proton NMR τ 1.9–2.8 (multiplet, phenyl). Anal. Calcd for $C_{45}H_{35}Cl_3NiP_2$: C, 67.3; H, 4.4; Cl, 13.2. Found: C, 67.1; H, 4.4; Cl, 13.2. This product is stable in air for a short period.

(5) L = $C_6H_5PCl_2$. A solution of 0.3 g (0.77 mmol) of $(C_6H_5)_3C_3Ni(CO)Cl$ in 10 mL of dichloromethane was treated with 0.30 g (1.69 mmol) of $C_6H_5PCl_2$ at room temperature. The orange solution was stirred for 5 min and then filtered. The filtrate was treated with 5 mL of hexane. Solvent was then evaporated at 25 °C (25 mm) to give very fine orange-yellow crystals. The supernatant liquid was removed with a syringe, and the crystals were washed twice with *n*-hexane to give 0.52 g (90% yield) of $(C_6H_5)_3C_3Ni(PCl_2C_6H_5)_2Cl$: mp 80 °C dec; proton NMR τ 2.0–2.8 (multiplet, phenyl). Anal. Calcd for $C_{33}H_{25}Cl_5NiP_2$: C, 55.1; H, 3.5; Cl, 24.6. Found: C, 55.2; H, 3.5; Cl, 24.6. This product is stable in air only for 0.5 h.

(6) L = Triphenyl Phosphite. A solution of 0.24 g (0.62 mmol) of $(C_6H_5)_3C_3Ni(CO)Cl$ in 10 mL of dichloromethane was treated with 0.42 g (1.35 mmol) of triphenyl phosphite at room temperature. After stirring of the mixture for 5 min, the orange solution was filtered. Solvent was evaporated from the filtrate at 25 °C (25 mm). The dark red oily residue was dissolved in 5 mL of tetrahydrofuran to give a slightly cloudy solution. Keeping this solution at -10 °C precipitated an orange solid which was filtered and washed with hexane to give 0.51 g (80% yield) of $(C_6H_5)_3C_3Ni[P(OC_6H_5)_3]_2Cl$: mp 108–113 °C; proton NMR τ 1.9–3.2 (multiplet, phenyl). Anal. Calcd for $C_{57}H_{45}ClNiO_6P_2$: C, 69.7; H, 4.6; Cl, 3.6. Found: C, 69.5; H, 4.6; Cl, 3.8. This product was stable in air for a short period.

(7) L = Triisopropyl Phosphite. A solution of 0.40 g (1.03 mmol) of $(C_6H_5)_3C_3Ni(CO)Cl$ in 20 mL of dichloromethane was treated with 0.51 g (2.47 mmol) of triisopropyl phosphite at room temperature. After stirring of the solution for 5 min, the reaction mixture was filtered. The filtrate was evaporated to dryness at 25 °C (25 mm). A solution of the residue in a minimum of warm heptane was kept overnight at -10 °C to give 0.42 g (50% yield) of dark red $(C_6H_5)_3C_3Ni[P(OCH(CH_3)_2)_3]_2Cl$: mp 120–122 °C; proton NMR τ 1.8–2.7 (multiplet, 15 H, phenyl), τ 5.0–5.6 (multiplet, 6 H, methylene), τ 8.90 (doublet, 36 H, methyl). Anal. Calcd for $C_{39}H_{36}ClNiO_6P_2$: C, 60.2; H, 7.4; Cl, 4.6. Found: C, 61.4; H, 7.3; Cl, 4.9. This product is stable in air for 0.5 h.

(8) L = Trimethyl Phosphite. A solution of 0.35 g (0.9 mmol) of $(C_6H_5)_3C_3Ni(CO)Cl$ in 10 mL of dichloromethane was treated with 0.24 g (2.0 mmol) of trimethyl phosphite at room temperature. The resulting mixture was stirred for 5 min and then filtered. The filtrate was treated with 5 mL of *n*-hexane. Solvent was removed from the resulting red solution at 25 °C (25 mm) until the solution became slightly cloudy. This solution was then cooled at -78 °C to give yellow-orange crystals. After the supernatant liquid was removed with a syringe, these crystals were washed with *n*-hexane to give 0.36 g (63% yield) of fairly air-stable $(C_6H_5)_3C_3Ni[P(OCH_3)_3]_2Cl$: mp 118–120 °C; proton NMR τ 1.8–2.7 (multiplet, 15 H, phenyl), τ 6.67 (doublet, 18 H, methyl). Anal. Calcd for $C_{27}H_{33}ClNiO_6P_2$: C, 53.2; H, 5.5; Cl, 5.8. Found: C, 53.0; H, 5.4; Cl, 5.7.

Isolation of the 1:1 Complex $(C_6H_5)_3C_3Ni[P(C_6H_5)_2CH_3]Cl$. A solution of 0.20 g (0.51 mmol) of $(C_6H_5)_3C_3Ni(CO)Cl$ in 10 mL of dichloromethane was treated with 0.10 g (0.51 mmol) of methyldiphenylphosphine at room temperature. This mixture was stirred for 10 min and then filtered. Solvent was removed from the red filtrate at 25 °C (25 mm). The slightly oily solid residue was treated with methanol. The supernatant liquid was removed with a syringe to give a fine red powder. The product was washed several times with methanol to give 0.28 g (90% yield) of $(C_6H_5)_3C_3Ni[P(C_6H_5)_2CH_3]Cl$: mp 150 °C dec; proton NMR τ 2.3–3.2 (multiplet, 25 H, phenyl), τ 8.64 (broad singlet, 3 H, methyl). Anal. Calcd for $C_{34}H_{28}ClNiP$: C, 72.7; H, 5.0; Cl, 6.3. Found: C, 72.8; H, 5.1; Cl, 6.2. Although this product was fairly air-stable, it could not be recrystallized without decomposition.

Catalytic Reactions and Their Analyses by Gas Chromatography. All catalytic reactions were carried out in dichloromethane solutions under nitrogen in a flask immersed in a temperature-controlled water bath using solutions of quadricyclane made according to the published procedure.[9] Samples periodically withdrawn were analyzed by gas chromatography using a 6 ft $\times$ $^1/_8$ in. 7.8% G.E. silicone oil on Chromosorb W (60/80) mesh stainless steel column at 75 °C and nitrogen as a carrier gas at 20–30 mL/min. The quantitative analyses of norbornadiene and quadricyclane were performed by comparing the areas of their gas chromatographic peaks with those of the solvents dichloromethane or benzene. Previous work[3] indicates that the response of the gas chromatography detector used was essentially identical for norbornadiene and quadricyclane.
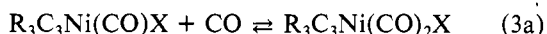
Results

Interconversions of (Triphenylcyclopropenyl)nickel Derivatives. When this project was started, available information on the chemistry of the (triphenylcyclopropenyl)nickel complexes $(C_6H_5)_3C_3Ni(CO)X$ (III: X = Cl and Br)[4] was very limited. The only reported derivatives of these nickel complexes were $[(C_6H_5)_3C_3Ni(NC_5H_5)_2Cl]\cdot NC_5H_5$[7] and $(C_6H_5)_3C_3NiC_5H_5$[8] made by the following reaction sequence:

$$(C_6H_5)_3C_3Ni(CO)Cl + 3C_5H_5N \rightarrow$$
$$[(C_6H_5)_3C_3Ni(NC_5H_5)_2Cl]\cdot NC_5H_5 + CO \quad (1)$$

$$[(C_6H_5)_3C_3Ni(NC_5H_5)_2Cl]\cdot NC_5H_5 + TlC_5H_5 \rightarrow$$
$$(C_6H_5)_3C_3NiC_5H_5 + TlCl + 3C_5H_5N \quad (2)$$
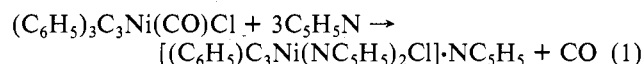
A related tri-*tert*-butylcyclopropenyl complex $[(CH_3)_3C]_3$-$C_3Ni(CO)Br$[5] had also been reported.

The triphenylcyclopropenyl complex $(C_6H_5)_3C_3Ni(CO)Cl$ was found to dissolve in a large excess of dichloromethane (3 mmol/L) to give an initial deep red solution, which upon being stirred gradually turns dark red-brown with release of CO, as confirmed by the disappearance of the originally observed 2055-cm^{-1} band in the $\nu(CO)$ region. The CO ligand in $(C_6H_5)_3C_3Ni(CO)Cl$ thus is labile in solution so that the complex rapidly loses CO at room temperature in a nitrogen stream. Concentration of the dichloromethane solution of $(C_6H_5)_3C_3Ni(CO)Cl$ after loss of the CO was found to give a dark red-brown solid, which was poorly soluble in chloroform, tetrahydrofuran, and benzene. The elemental analysis on this product did not correspond to the expected stoichiometry $(C_6H_5)_3C_3NiCl$ but instead to the stoichiometry $6(C_6H_5)_3C_3NiCl\cdot NiCl_2$ suggesting that the halogenated solvent dichloromethane is not completely inert but leads to some oxidation of the nickel with loss of triphenylcyclopropenyl rings. The structure of this product remains unknown since the solid did not form suitable single crystals for X-ray crystallography and conventional spectroscopic methods gave little useful information other than confirming, through infrared spectroscopy, the expected absence of nickel carbonyl groups.

Infrared spectra of the tri-*tert*-butylcyclopropenyl complexes[5] were reported to indicate the presence of equilibria 3a and 3b. The various components were identified by the following $\nu(CO)$ frequencies:[5] $[(CH_3)_3C]_3C_3Ni(CO)Br$, 2055 cm^{-1}; $[(CH_3)_3C]_3C_3Ni(CO)_2Br$, 2060 and 2089 cm^{-1}; and $Ni(CO)_4$, 2044 cm^{-1}. In our hands treatment of a freshly prepared dichloromethane solution of the triphenylcyclopropenyl complex $(C_6H_5)_3C_3Ni(CO)Cl$ with CO was found to result in the appearance of new bands at 2045 and 2070 cm^{-1} which can be assigned to $(C_6H_5)_3C_3Ni(CO)_2Cl$. More prolonged treatment with CO results ultimately in the disappearance of both of these new bands as well as the original 2055-cm^{-1} band of $(C_6H_5)_3C_3Ni(CO)Cl$ with the appearance of a single sharp band at 2049 cm^{-1} which can be assigned to

$$R_3C_3Ni(CO)X + CO \rightleftharpoons R_3C_3Ni(CO)_2X \quad (3a)$$

$$R_3C_3Ni(CO)_2X + 2CO \rightleftharpoons Ni(CO)_4 + [R_3C_3]X \quad (3b)$$

**Table I.** Phosphorus-31 NMR Spectra of the Complexes $(C_6H_5)_3C_3NiL_2Cl$

| L^a	chemical shifts, δ^b	coordination chemical shifts^d
$P(C_6H_5)_2CH_3{}^c$	−7.9	−36
$P(OCH_3)_3$	−150.4	−9
$P(O\text{-}i\text{-}C_3H_7)_3$	−143.8	−7
$P(C_6H_5)Cl_2$	−165.3	−3
$P(OC_6H_5)_3$	−129.3	−2

^{a} The chemical shifts of the free ligands are reported in M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer in "Topics in Phosphorus Chemistry", Vol. 5, Interscience, New York, 1967. ^{b} ^{31}P NMR spectra were recorded in CH_2Cl_2 solutions. H_3PO_4 was used as an internal standard. Positive numbers refer to upfield chemical shifts. ^{c} The chemical shift of $(C_6H_5)_3C_3Ni[P(C_6H_5)_2CH_3]Cl$ is δ −7.2. ^{d} This corresponds to $\delta[(C_6H_5)_3C_3NiL_2Cl] - \delta(L)$ in ppm.

$Ni(CO)_4$ on the basis of a comparison with the spectrum of pure $Ni(CO)_4$ in dichloromethane. The carbonyl-free complex of stoichiometry $6(C_6H_5)_3C_3NiCl\cdot NiCl_2$ in dichloromethane reacts with CO to form initially $(C_6H_5)_3C_3Ni(CO)Cl$ as indicated by the appearance of its 2055-cm^{-1} $\nu(CO)$ frequency. Further treatment of the resulting solution with CO results in the same spectral changes as found in the reaction of $(C_6H_5)_3C_3Ni(CO)Cl$ with CO discussed above indicating again reactions 3a and 3b (R = C_6H_5, X = Cl). These experimental observations indicate facile interconversions of (triphenyl-cyclopropenyl)nickel chloride complexes with different CO:Ni ratios.

Dichloromethane solutions of $(C_6H_5)_3C_3Ni(CO)Cl$ also react with oxygen, phosphorus, and nitrogen donor ligands (L) such as tetrahydrofuran, phosphines, phosphites, and pyridine derivatives to give new complexes of the type $(C_6H_5)_3C_3NiL_2Cl$ (IV) with a 2:1 L:Ni ratio. The tetrahydrofuran complex $(C_6H_5)_3C_3Ni(OC_4H_8)_2Cl$ (IV: L = tetrahydrofuran) was

IV
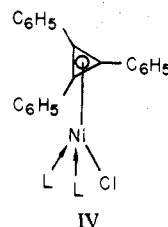
prepared by dissolving $(C_6H_5)_3C_3Ni(CO)Cl$ in a large amount of tetrahydrofuran or in dichloromethane in the presence of tetrahydrofuran and then removing the evolved CO under vacuum. The corresponding reactions of $(C_6H_5)_3C_3Ni(CO)Cl$ with phosphorus and nitrogen donors are much faster. Addition of 2,2'-bipyridyl, $CH_3P(C_6H_5)_2$, $C_6H_5PCl_2$, $(C_6H_5)_2PCl$, $(C_6H_5O)_3P$, $[(CH_3)_2CHO]_3P$, or $(CH_3O)_3P$ to a dichloromethane suspension of $(C_6H_5)_3C_3Ni(CO)Cl$ at room temperature results in instant CO evolution to give a clear red solution after a few minutes. From such solutions new complexes of the type $(C_6H_5)_3C_3NiL_2Cl$ could be isolated which are air sensitive, particularly in solution, and decompose upon heating under nitrogen to black solids insoluble in organic solvents. The increasing order of stability of the isolated $(C_6H_5)_3C_3NiL_2Cl$ complexes for different ligands L is as follows: tetrahydrofuran < $C_6H_5PCl_2$ < $(C_6H_5)_2PCl$ < $(C_6H_5O)_3P$ < $(CH_3O)_3P$ < $[(CH_3)_2CHO]_3P$ < $CH_3P(C_6H_5)_2$ < 2,2'-bipyridyl. These trends in the thermal stability of the $(C_6H_5)_3C_3NiL_2Cl$ complexes (IV) correlate approximately with the electron-donating power of the ligand L and with the coordination chemical shifts in the phosphorus-31 NMR spectra (Table I) in the cases of the trivalent phosphorus ligands. The observation of one singlet resonance in the phosphorus-31 NMR spectra of each of the complexes

(C₆H₅)₃C₃Ni(CO)Cl : (△), 4.5mM; (×), 3.0mM; (○), 1.5mM; (●), 0.60mM.
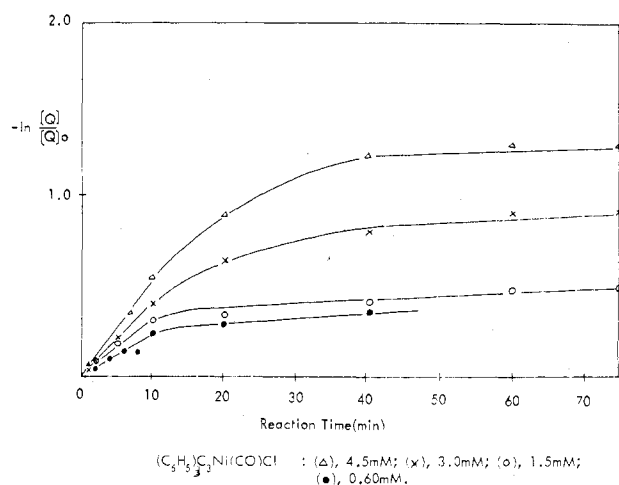
Figure 1. Plot of $-\ln$ ([quadricyclane]/[quadricyclane]$_{t=0}$) vs. reaction time for different concentrations of the catalyst $(C_6H_5)_3C_3Ni(CO)Cl$ at 0 °C.

$(C_6H_5)_3C_3NiL_2Cl$ (L = trivalent phosphorus ligand) suggests that both trivalent phosphorus ligands are equivalent in accord with distorted tetrahedral structures IV similar to that found by X-ray crystallography for the pyridine complex $(C_6-H_5)_3C_3Ni(NC_5H_5)_2Cl\cdot NC_5H_5$.[7]

Attempts were also made to prepare complexes of the stoichiometry $(C_6H_5)_3C_3NiLCl$ with a 1:1 L:Ni ratio. However, only $(C_6H_5)_3C_3Ni[P(C_6H_5)_2CH_3]Cl$ could be obtained reasonably pure despite the fact that all of the monodentate trivalent phosphorus ligands listed above were tried in such reactions. This complex was identified by its elemental analysis, proton NMR spectrum, and a higher decomposition temperature (150 °C) than that of the corresponding 2:1 L–Ni complex $(C_6H_5)_3C_3Ni[P(C_6H_5)_2CH_3]_2Cl$ (140 °C). The ability to isolate a pure 1:1 Li–Ni complex from methyldiphenylphosphine but not from the other trivalent phosphorus ligands may relate to the fact that among the 2:1 L–Ni complexes prepared from trivalent phosphorus ligands listed above, the complex derived from methyldiphenylphosphine was found to exhibit the highest thermal stability.

The reaction of $(C_6H_5)_3C_3Ni(CO)Cl$ with norbornadiene (I), a chelating diolefin, is of interest in connection with the use of this nickel complex as a catalyst for the conversion of quadricyclane (II) to norbornadiene. However, treatment of the complex $(C_6H_5)_3C_3Ni(CO)Cl$ with norbornadiene did not result in any change after 1 day at room temperature. Furthermore, the expected product $(C_6H_5)_3C_3Ni(C_7H_8)Cl$ was not isolated even after adding norbornadiene to a dichloromethane solution of $(C_6H_5)_3C_3Ni(CO)Cl$ after having allowed the CO to escape to generate the carbonyl-free complex (see above). Apparently, the electron-donating power of norbornadiene is too weak to form a stable $(C_6H_5)_3C_3Ni(C_7H_8)Cl$ complex in accord with the trends noted above for the stabilities of $(C_6H_5)_3C_3NiL_2Cl$ complexes derived from trivalent phosphorus ligands of widely different electron-donating powers.

Reactions of $(C_6H_5)_3C_3Ni(CO)Cl$ in dichloromethane solution with various Grignard reagents, alkyl- and aryllithium derivatives, and potassium carboxylates all were found to give dark red-brown reaction solutions, from which dark gray solids precipitated upon addition of hexane. These solids have neither CO nor alkyl or aryl groups bonded to nickel as indicated by infrared and proton NMR spectra. The constitution of these solids is not known in detail, although they serve as fairly active catalysts for the conversion of quadricyclane to norbornadiene.

(Triphenylcyclopropenyl)nickel Derivatives as Catalysts for the Conversion of Quadricyclane to Norbornadiene. Figures 1 and 2 are plots of $-\ln$ ([quadricyclane]/[quadricyclane]$_{t=0}$)

Quadricyclane : (△), 0.48M; (×), 0.23M; (○), 0.096M; (●), 0.019M.
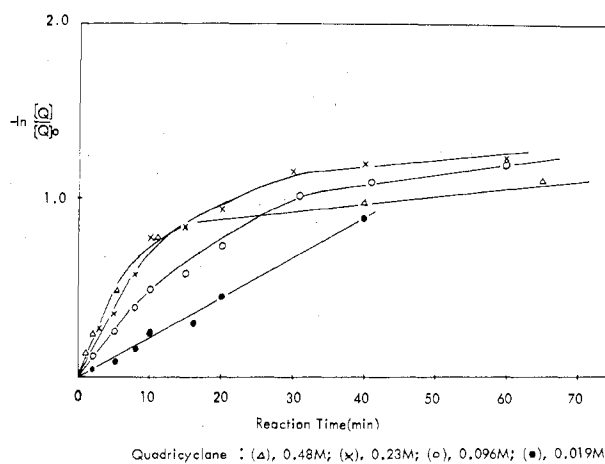
Figure 2. Plot of $-\ln$ ([quadricyclane]/[quadricyclane]$_{t=0}$) vs. reaction time for different initial concentrations of quadricyclane at 0 °C.

Table II. $(C_6H_5)_3C_3Ni(CO)Cl$ as a Catalyst for the Conversion of Quadricyclane to Norbornadiene[a]

catalyst concn, mol/L × 10⁻³	initial quadricyclane concn, mol/L	reaction temp, °C	rate const, L (mol of cat.)⁻¹ s⁻¹
0.60	0.14	30	3.9
1.5	0.14	30	2.5
3.0	0.14	30	2.2
4.5	0.14	30	1.9
0.60	0.15	0	0.67
1.5	0.15	0	0.39
3.0	0.15	0	0.24
4.5	0.15	0	0.21
4.5	0.48	0	0.34
4.5	0.23	0	0.29
4.5	0.096	0	0.17
4.5	0.019	0	0.093

[a] Solvent CH_2Cl_2.

vs. reaction time at 0 °C under different initial concentrations of $(C_6H_5)_3C_3Ni(CO)Cl$ and quadricyclane. Table II summarizes the rate constants at $t = 0$ under various conditions. These results show that the complex $(C_6H_5)_3C_3Ni(CO)Cl$ is a very active catalyst for the conversion of quadricyclane to norbornadiene under mild conditions. The initial rates depend on the concentration of the catalyst (Figure 1) and quadricyclane (Figure 2). The rate decrease begins after a certain reaction period to give ultimately a constant rate. In particular, in reactions at different concentrations of the catalyst, the rates after the reaction reaches a steady state are almost identical.

A possible explanation for this reduction in rate as the reaction proceeds is coordination of norbornadiene to the catalyst thereby blocking some of the coordination sites needed for the catalytic action. In order to check this possibility, some catalytic runs were performed in the presence of added norbornadiene (Figure 3 and Table III). The slope of the $-\ln$ ([quadricyclane]/[quadricyclane]$_{t=0}$) plot vs. time was found to remain approximately constant until the value for the mole ratio of the norbornadiene formed catalytically to the catalyst concentration approaches 15–20. At this point the slope gradually decreases, indicating a decreasing rate of quadricyclane disappearance. Moreover, the effect of the presence of norbornadiene is not sufficient to rationalize the retardation of the rates since the effect of added norbornadiene on the rate is not significant even if the initial mole ratio of [norbornadiene]/[catalyst] (Table III and Figure 3) is 60, a factor of approximately 3 times that of the experimentally observed value of 15–20. The possible explanation of only weak adduct formation of norbornadiene with the catalyst is supported by

Table III. Effect of Added Norbornadiene on the Reaction Rates for the Conversion of Quadricyclane to Norbornadiene with a $(C_6H_5)_3C_3Ni(CO)Cl$ Catalyst[a]

initial norborn-adiene concn, mol/L	initial quadri-cyclane concn, mol/L	catalyst concn, mol/L × 10⁻³	rate const, L (mol of cat.)⁻¹ s⁻¹
7.7	0.096	4.5	0.008
1.1	0.096	4.5	0.034
0.28	0.096	4.5	0.10
0.11	0.096	4.5	0.17

[a] Reaction temperature 0 °C, solvent CH_2Cl_2.

Norbornadiene : (--), 0.0005M; (o), 0.11M; (x), 0.28M; (△), 1.1M.
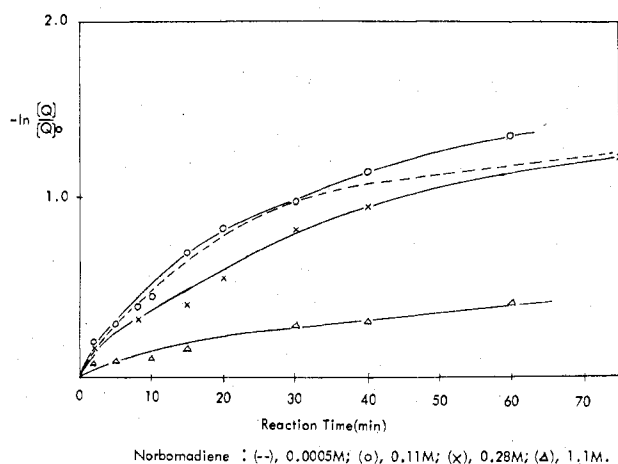
Figure 3. Plot of $-\ln$ ([quadricyclane]/[quadricyclane]$_{t=0}$) vs. reaction time for different initial concentrations of norbornadiene at 0 °C.

the inability to isolate a pure sample of $(C_6H_5)_3C_3Ni(C_7H_8)Cl$ or other norbornadienenickel complex upon treatment of $(C_6H_5)_3C_3Ni(CO)Cl$ with norbornadiene as discussed above.

An infrared spectrum of a solution obtained by mixing $(C_6H_5)_3C_3Ni(CO)Cl$ with excess quadricyclane in dichloromethane shows no $\nu(CO)$ frequencies suggesting that the catalytically active nickel species contains no carbonyl groups. Furthermore, in a CO atmosphere the rate of conversion of quadricyclane to norbornadiene catalyzed by $(C_6H_5)_3C_3$-Ni(CO)Cl was found to decrease to one-fourth of the rate in a nitrogen atmosphere. This is consistent with the coordination of CO to the catalyst to give ultimately $(C_6H_5)_3C_3Ni(CO)_2Cl$ and $Ni(CO)_4$, which have no vacant sites for quadricyclane coordination thereby leading to catalyst poisoning.

The catalytic activity of the bromide $(C_6H_5)_3C_3Ni(CO)Br$ was found to be about one-eighth of that of the corresponding chloride under comparable conditions (i.e., a rate constant of 0.33 L (mol of catalyst)⁻¹ s⁻¹ at 30 °C, 0.15 mol/L initial quadricyclane concentration, and 0.0015 mol/L catalyst concentration as compared with a rate constant of 2.5 L (mol of catalyst)⁻¹ s⁻¹ for the corresponding chloride complex under comparable conditions). The cyclopentadienyl derivative $(C_6H_5)_3C_3NiC_5H_5$ was found to be catalytically inactive under comparable conditions.

The catalytic activities of the new $(C_6H_5)_3C_3NiL_2Cl$ complexes have also been measured as well as those of mixtures of stoichiometries $(C_6H_5)_3C_3NiLCl$ and $(C_6H_5)_3C_3NiL_3Cl$ generated in situ by mixing the ligand and $(C_6H_5)_3C_3$-Ni(CO)Cl in 1:1 and 3:1 L:Ni ratios, respectively (Table IV). For any ligand L the rates decrease as the L:Ni ratio increases from 1:1 to 3:1 consistent with the additional ligands blocking coordination sites needed for catalytic activity. Furthermore, in the case of the $(C_6H_5)_3C_3NiL_2Cl$ catalysts, the rates decrease as the phosphorus-31 coordination chemical shift (Table I) increases thereby indicating, as expected, that the stronger the metal–ligand bonds, the more difficult the ligand disso-

Table IV. The Rate Constants for the Conversion of Quadricyclane to Norbornadiene in the Presence of $(C_6H_5)_3C_3NiL_nCl$[a]

	rate const, L (mol of Ni)⁻¹ s⁻¹		
L	$n = 1$	$n = 2$	$n = 3$
tetrahydrofuran		0.37	
$P(OC_6H_5)_3$	1.0	0.22	0.11
$P(C_6H_5)Cl_2$	0.19	0.11	0.039
$P(C_6H_5)_2Cl$	0.19	0.066	0.034
$P[OCH(CH_3)_2]_3$	0.11	0.022	0.0053
$P(OCH_3)_3$	0.055	0.014	0.0021
$P(C_6H_5)_2CH_3$	0.059	0.0035	0.000
pyridine			0.000
bipyridine	0.000		

[a] Reaction temperature 30 °C, solvent CH_2Cl_2; nickel concentration 0.0015 mol/L; initial quadricyclane concentration 0.58 mol/L.

ciation. In general, the catalytic activities of the $(C_6H_5)_3$-C_3NiL_2Cl derivatives (Table IV) appear to be appreciably less than that of $(C_6H_5)_3C_3Ni(CO)Cl$.

Discussion

The results described in this paper indicate that the nickel complex $(C_6H_5)_3C_3Ni(CO)Cl$ (III: X = Cl) readily loses its CO ligand under the conditions where it catalyzes the isomerization of quadricyclane (II) and norbornadiene (I). This suggests that such reactions involve a catalytically active carbonyl-free complex $[(C_6H_5)_3C_3NiCl]_2$ (V: R = C_6H_5, X = Cl) analogous to the reported[9] tri-*tert*-butylcyclopropenyl derivative $\{[(CH_3)_3C]_3C_3NiBr\}_2$ (V: R = $(CH_3)_3C$, X = Br) and the well-known[10] [(η^3-allylic)NiX]$_2$ derivatives (VI). If
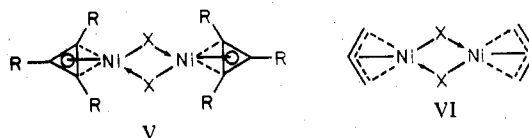
in V the cyclopropenyl rings are *formally* regarded as four-electron donor cyclopropenyl anions, then they can be considered as bidentate ligands so that $[R_3C_3NiX]_2$ species may be regarded as containing square-planar nickel(II). Their catalytic activities for the conversion of quadricyclane (II) to norbornadiene (I) thus correspond to the similar catalytic activities of a variety of other square-planar complexes of late transition metals such as those of rhodium(I),[11] palladium-(II),[11,12] iron(II),[13] cobalt(II),[13] and nickel(II).[13] The relatively high catalytic activity of the (triphenylcyclopropenyl)nickel system compared to most other square-planar nickel(II) derivatives may relate to the tendency for the cyclopropenyl ring to acquire a positive charge as in the cyclopropenyl cation thereby making the nickel atom relatively negative and thus as susceptible as a typical nickel(0) derivative toward oxidative addition. In other words, the nickel atom in $(C_6H_5)_3C_3Ni$-(CO)X and related cyclopropenylnickel halide derivatives may be sterically like nickel(II) and electronically like nickel(0) because of the unusual characteristics of the cyclopropenyl ring.

Registry No. I, 121-46-0; II, 278-06-8; III (X = Cl), 69120-62-3; $(C_6H_5)_3C_3NiCl$, 69120-63-4; $(C_6H_5)_3C_3Ni(OC_4H_8)_2Cl$, 69120-64-5; $(C_6H_5)_3C_3Ni(N_2C_{10}H_8)Cl$, 69120-65-6; $(C_6H_5)_3C_3Ni[P(OC_6H_5)_3]_2Cl$, 69120-66-7; $(C_6H_5)_3C_3Ni[P(OCH(CH_3)_2)_3]_2Cl$, 69120-67-8; $(C_6H_5)_3C_3Ni[P(OCH_3)_3]_2Cl$, 69120-68-9; $(C_6H_5)_3C_3Ni[P(C_6$-

$H_5)_2CH_3]Cl$, 69120-69-0; $(C_6H_5)_3C_3Ni[P(C_6H_5)Cl_2]_2Cl$, 69120-70-3; $(C_6H_5)_3C_3Ni[P(OC_6H_5)_3]Cl$, 69120-71-4; $(C_6H_5)_3C_3Ni[P(C_6H_5)-Cl_2]Cl$, 69120-72-5; $(C_6H_5)_3C_3Ni[P(C_6H_5)_2Cl]Cl$, 69120-73-6; $(C_6H_5)_3C_3Ni[P(OCH(CH_3)_2)_3]Cl$, 69120-74-7; $(C_6H_5)_3C_3-Ni[P(OCH_3)_3]Cl$, 69120-75-8; $(C_6H_5)_3C_3Ni[P(C_6H_5)_2Cl]_2Cl$, 69120-73-6; $(C_6H_5)_3C_3Ni[P(C_6H_5)_2CH_3]_2Cl$, 69177-57-7; $(C_6-H_5)_3C_3Ni[P(OC_6H_5)_3]_3Cl$, 69120-76-9; $(C_6H_5)_3C_3Ni[P(C_6H_5)Cl_2]_3Cl$, 69120-77-0; $(C_6H_5)_3C_3Ni[P(C_6H_5)_2Cl]_3Cl$, 69120-78-1; $(C_6H_5)_3-C_3Ni[P(OCH(CH_3)_2)_3]_3Cl$, 69120-79-2; $(C_6H_5)_3C_3Ni[P(OCH_3)_3]_3Cl$, 69120-80-5.

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UV Photoelectron Study of Mononuclear Metal Complexes of Methylaminobis(difluorophosphine)

MARCO V. ANDREOCCI, CARLA CAULETTI, CLAUDIO FURLANI, and R. BRUCE KING*

Gas-phase UV photoelectron spectra are reported of the title ligand L, of its mononuclear ML_3 complexes (M = Cr, Mo, W), and of the polynuclear Ni and Rh complexes. Ionization of the d^6 system of ML_3 occurs at relatively low IE between ca. 7.7 and 7.9 eV. An assignment is proposed for the higher ionization processes, covering coordinative σ_{MP}, N lone pair, σ_{CH} and σ_{NP}, and fluorine σ and π orbitals.

Introduction

The mononuclear tris-chelate complexes of the d^6 metals Cr, Mo, and W with methylaminobis(difluorophosphine) (L), first reported[1] in 1977, and the polynuclear complexes of Ni and Rh have been investigated by UV photoelectron spectroscopy in the gas phase. Their spectra are generally well resolved and yield clear, even if not always detailed, information about the electronic structure of the valence shell, including the energy position of metal d orbitals, of the σ-bonding coordination orbitals, and of the electron lone pairs present in the ligand structure. Comparisons and structural correlations can be drawn and will be discussed in the next sections, with other volatile complexes of zerovalent metals, particularly with carbonyls and PF_3 complexes of d^6 elements.

Experimental Section

The free ligand $CH_3N(PF_2)_2$ is a highly volatile liquid,[2] and its photoelectronic spectrum was recorded from liquid samples. CrL_3, MoL_3, WL_3, $[NiL_2]_n$, and Rh_4L_6 were prepared according to previous literature reports[1,4] and proved sufficiently volatile for measurements as solid samples in the photoelectron spectrometer. For the Ni compound, "n" is known to be predominantly 2 in the gas phase from mass spectral measurements.[3] Approximate temperatures required to obtain spectra of good intensity at the internal pressure of the spectrometer were 60 °C for CrL_3, 65–70 °C for MoL_3, 90 °C for WL_3, 125 °C for $[NiL_2]_n$, and 210 °C for Rh_4L_6. The Cr, Mo, and W compounds appeared to be completely stable, leaving no residue after sublimation; and are assumed to be present in the gas phase in the same mononuclear pseudooctahedral structure assigned to them in the solid state. The Ni and Rh complexes are accompanied by consistent traces of water and left decomposed, solid residues after photoelectronic measurements.

Photoelectronic spectra were taken on a Perkin-Elmer PS 18 photoelectron spectrometer with the use of He I 584-Å radiation in the presence of Ar and CH_3I as calibrant gases. The Cr and W complexes were also measured with He II 304-Å radiation, which however does not produce in the present case any remarkable change in the peak intensity. Reproducibility of the spectra was in any case excellent, provided the temperature, whose effect is critical, was kept

constant to better than ca. 2 °C; instrumental resolution was typically 40 meV at the Ar doublet energy (15.76–15.94 eV IE). All substances exerted a moderate attack on the internal walls of the spectrometer, resulting in slight contamination after each run.

Results

The free ligand $CH_3N(PF_2)_2$ has, in the low IE region, a composite band with maximum at 10.95 and shoulder at 11.45 eV (approximate intensity ratio 2:1) that is in the region where ionization of the lone pairs of N and P are expected (see Table I and Figure 1). The ionization of the P lone pairs appears at 12.31 eV in PF_3 and 10.50 eV in $(CH_3)_2N-PF_2$.[6,7] Since the electronegativity of the surrounding groups around P is very similar in $(CH_3)_2N-PF_2$ and $CH_3N(PF_2)_2$, and just slightly larger in the latter case, assignment of the 10.95-eV band component in $CH_3N(PF_2)_2$ to n_P seems plausible. The N lone-pair ionization in $(CH_3)_2N-PF_2$ is at 9.60 eV but is expected to shift considerably to higher values in $CH_3N(PF_2)_2$, where nitrogen has two highly electronegative $-PF_2$ neighbors instead of one and can thus be identified as the 11.45-eV component.

Another support to this assignment comes from the comparison with NH_2-PF_2, whose UV PES is reported and assigned in ref 7. This spectrum has two bands in the energy region of the N and P lone pairs which the authors[7] relate in order of increasing energy to the n_N, at 10.7 eV (this vertical IE is the same as in NH_3), and to the n_P, at 11.5 eV, on the grounds of the fact that the two lone pairs do not interact, being orthogonal to each other. We propose an alternative assignment, where the IE of the N lone pair is instead identified with the 11.5-eV band, i.e., at a higher value with respect to NH_3, due to the $-PF_2$ group being more electronegative than the H atom and exerting its inductive effect even if the N and P lone pairs do not interact directly.

This implies a reverse order of energy levels, with the n_P^{-1} ionization at 10.9 eV and the n_N^{-1} at 11.5 eV. Now these values are equal to those proposed by us for the n_N and n_P ionizations of the $(PF_2)_2NCH_3$ molecule, which implies that the $-PF_2$ and $-CH_3$ groups, which replace two H atoms in

* To whom correspondence should be addressed at the University of Georgia.