Inorg. Chem. **1980**, *19*, 2441–2448 **2441**

Contribution from the Department of Chemistry,
Northwestern University, Evanston, Illinois 60201

Synthesis and Characterization of Some π-Bonded Diazo Complexes of Nickel(0), Platinum(0), and Ruthenium(0): Molecular Structure of $Ru(CO)_2(N_2C_5Cl_4)(P(C_6H_5)_3)_2 \cdot CH_2Cl_2$

K. DAHL SCHRAMM and JAMES A. IBERS*

Received September 27, 1979

A series of diazo complexes with the compositions $M(N_2R)L_2$ (M = Ni, L = *t*-BuNC; M = Pt, L = PPh_3; N_2R = $N_2C_5Cl_4$, $N_2C_5Br_4$) and $Ru(CO)_2(N_2R)(PPh_3)_2$ (N_2R = $N_2C_5Cl_4$, $N_2C_5Br_4$, 9-diazofluorene, or 2,7-dibromo-9-diazofluorene) has been prepared by the direct reaction of the given neutral diazo molecule with an appropriate transition-metal system. The complexes have been characterized spectroscopically and in the case of $Ru(CO)_2(N_2C_5Cl_4)(PPh_3)_2 \cdot CH_2Cl_2$ crystallographically. In this complex the tetrachlorodiazocyclopentadiene molecule is coordinated to the Ru atom in the η^2 fashion. Some relevant metrical parameters are Ru–N(1) = 2.062 (4) Å, Ru–N(2) = 2.141 (5) Å, Ru–P(1) = 2.390 (2) Å, Ru–P(2) = 2.385 (2) Å, Ru–C(CO) = 1.886 (6) and 1.925 (6) Å, N(1)–N(2) = 1.224 (6) Å, N(1)–C(1) = 1.372 (7) Å, P(1)–Ru–P(2) = 168.80 (5)°, C–Ru–C(carbonyl) = 95.1 (2)°, N(1)–Ru–N(2) = 33.8 (2)°, and N(1)–N(2)–C(1) = 131.6 (5)°. The compound crystallizes with four formula units in the monoclinic space group C_{2h}^5-$P2_1/c$ in a cell of dimensions a = 14.66 (1) Å, b = 10.891 (7) Å, c = 26.73 (2) Å, and β = 94.11 (2)°. On the basis of 5728 unique reflections collected at −159 °C the structure was refined by full-matrix, least-squares techniques to a final value of the conventional R index of 0.057. The entire series of complexes shows a reduction of the N–N stretching frequency from ca. 2100 cm^{-1} in the free diazo molecules to ca. 1500 cm^{-1} in these complexes. The correspondence of these reduced stretching frequencies strongly suggests that in each of these complexes the diazo molecule has η^2 coordination to the transition metal and may be described as π bound through the N–N multiple bond. Although the complexes $Ni(N_2R)(PPh_3)_2$ (N_2R = $N_2C_5Cl_4$, $N_2C_5H_4$) could not be isolated, they were generated in situ from $Ni(C_2H_4)(PPh_3)_2$ and the diazo molecule. Reaction of these diazo complexes with diethyl maleate at 100 °C did not produce cyclopropanation products; however with the $N_2C_5H_4$ complex, an ylide, (triphenylphosphonium)cyclopentadienylidene, was obtained.

Introduction

The structural, synthetic, and reaction chemistry of neutral diazo molecules, N_2R, with transition metals is just beginning to develop despite the multitude of N_2R molecules in the literature. Studies carried out thus far indicate a rich and varied chemistry.[1-7] The obvious relation of transition-metal–N_2R complexes to those involving the more heavily utilized aryldiazo ligands, N_2R^+, as well as those with dinitrogen or nitrosyl ligands,[8] is a motivation for such studies. But reactions between N_2R molecules and transition-metal species do not always yield isolable complexes in which N_2R is a ligand. Indeed, facile loss of dinitrogen from such molecules is an attractive synthetic route to carbene complexes.[9] There clearly is a need to explore the conditions under which isolable complexes involving N_2R molecules as ligands may be obtained and to correlate structure of such complexes with reaction chemistry. Comparison of the structures and reactions of such complexes with those of the related complexes of N_2R^+ will ultimately prove to be especially useful in understanding this chemistry.

In this paper we present the syntheses of a class of Ni(0), Pt(0), and Ru(0) complexes of diazo molecules in which the diazo molecule is shown to coordinate in the η^2 or "π-bonded" manner, a geometry known previously for only one other such complex and not at all for complexes of aryldiazo ligands, N_2R^+.

Experimental Section

All reactions were performed in freshly distilled solvents under a nitrogen atmosphere. Typical reactions involved ca. 0.1 mmol of metal complexes. Elemental analyses were performed by H. Beck of the Northwestern University Analytical Services Laboratory and by Micro-Tech Laboratories Inc., Skokie, Ill. The results of these analyses appear in Table I. Infrared spectra were obtained on Perkin-Elmer 283 and Nicolet 7199 FT-IR spectrometers as Nujol and Fluorolube mulls. Proton NMR spectra were obtained on a Varian CFT-20 NMR spectrometer, and the ^{31}P NMR spectra were obtained on a JEOL FX90Q NMR spectrometer, using Me_4Si and 85% phosphoric acid as the respective external reference standards. The proton and phosphorus NMR spectra were obtained at −55 °C by using $CDCl_3$ as the solvent. Infrared and NMR spectral data are contained in Table II.

Starting Materials. Literature methods were used for the preparation of "Ni(*t*-BuNC)$_2$",[10,11] $Pt(C_2H_4)(PPh_3)_2$,[12] 2,3,4,5-tetrachlorodiazocyclopentadiene,[4] 2,3,4,5-tetrabromodiazocyclopentadiene,[13] 9-diazofluorene,[14] and 2,7-dibromo-9-diazofluorene.[15]

Preparation of $Ni(C_2H_4)(PPh_3)_2$. $Ni(COD)_2$,[16] 0.174 g (0.63 mmol), and PPh_3, 0.332 g (1.26 mmol), were suspended in diethyl ether to form a deep red solution of "$Ni(PPh_3)_2$". Bubbling of ethylene through this solution caused an immediate color change from red to yellow, and upon cooling of the solution to 0 °C, yellow crystalline solid was obtained. This solid was filtered under nitrogen, dried in vacuo, and stored under an atmosphere of argon.

Preparation of $Ru(CO)_2(C_2H_4)(PPh_3)_2$. This compound was prepared by a modification of the literature procedures.[17,18] The

---

(1) (a) Otsuka, S.; Nakamura, A.; Koyama, T.; Tatsuno, Y. *Justus Liebigs Ann. Chem.*, **1975**, 626–35. (b) Nakamura, A.; Yoshida, T.; Cowie, M.; Otsuka, S.; Ibers, J. A. *J. Am. Chem. Soc.* **1977** *99*, 2108–17.

(2) (a) Herrmann, W. A. *Angew Chem., Int. Ed. Engl.* **1974**, *13*, 599. (b) Herrmann, W. A. *J. Organomet. Chem.* **1975**, *84*, C25–7. (c) Herrmann, W. A.; Ziegler, M. L.; Weidenhammer, K. *Angew Chem., Int. Ed. Engl.* **1976**, *15*, 368–9. (d) Herrmann, W. A. *Ibid.* **1978**, *17*, 800–12.

(3) (a) Herrmann, W. A. *Angew Chem., Int. Ed. Engl.* **1974**, *13*, 335–6. (b) Herrmann, W. A. *Chem. Ber.* **1975**, *108*, 486–99. (c) Redhouse, A. D. *J. Organomet. Chem.* **1975**, *99*, C29–30. (d) Redhouse, A. D.; Herrmann, W. A. *Angew Chem., Int. Ed. Engl.* **1976**, *15*, 615–6.

(4) Reimer, K. J.; Shaver, A. *Inorg. Chem.* **1975**, *14*, 2707–16; *J. Organomet. Chem.* **1975**, *93*, 239–52.

(5) (a) Herrmann, W. A.; Reiter, B.; Biersack, H. *J. Organomet. Chem.* **1975**, *97*, 245–51. (b) Herrmann, W. A.; Krüger, C.; Goddard, R.; Bernal, I. *J. Organomet. Chem.* **1977**, *140*, 73–89; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 334.

(6) Schramm, K. D.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3287–93.

(7) Schramm, K. D.; Ibers, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 2932–3.

(8) Sutton, D. *Chem. Soc. Rev.* **1975**, *4*, 443–70.

(9) Cardin, D. J.; Cetinkaya, B.; Doyle, M. J.; Lappert, M. F. *Chem. Soc. Rev.* **1973**, *2*, 99–144.

(10) Otsuka, S.; Nakamura, A.; Tatsuno, Y. *J. Am. Chem. Soc.* **1969**, *91*, 6994–9.

(11) Abbreviations: Ph = phenyl; *t*-BuNC = *tert*-butyl isocyanide; COD = 1,5-cyclooctadiene; COT = cyclooctatetraene.

(12) Hartley, F. R. *Organomet. Chem. Rev., Sect. A* **1970**, *6*, 119–37.

(13) Cram, D. J.; Partos, R. D. *J. Am. Chem. Soc.* **1963**, *85*, 1273–7.

(14) Schönberg, A.; Awad, W. I.; Latif, N. *J. Chem. Soc.* **1951**, 1368–9.

(15) Murahashi, S.; Moritani, I.; Nagai, T. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1655–60.

(16) Wilke, G. *Angew. Chem.* **1960**, *72*, 581–2.

(17) Cavit, B. E.; Grundy, K. R.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1972**, 60–61. Roper, W. R., private communication.

0020-1669/80/1319-2441$01.00/0 © 1980 American Chemical Society

Table I. Analytical Data for New Diazo Complexes of Ni(0), Pt(0), and Ru(0)

complex	color	% C[a] calcd	% C[a] found	% H calcd	% H found	% N calcd	% N found	% Cl or Br calcd	% Cl or Br found
$Ni(N_2C_5Cl_4)(t\text{-}BuNC)_2$ (I)	yellow-green	39.59	39.77	3.95	3.82	12.32	11.13		
$Ni(N_2C_5Br_4)(t\text{-}BuNC)_2$ (II)	dark green	28.47	27.58	2.85	2.93	8.56	8.22		
$Pt(N_2C_5Cl_4)(PPh_3)_2$ (III)	yellow	51.84	51.83	3.16	3.46	2.95	2.55	14.94	15.47
$Pt(N_2C_5Br_4)(PPh_3)_2$ (IV)	yellow	43.67	43.80	2.66	2.63	2.49	1.84	28.37	27.86
$Ru(CO)_2(N_2C_5Cl_4)(PPh_3)_2\cdot CH_2Cl_2$ (V)	yellow-orange	53.03	53.26	3.24	3.29	2.81	2.75	18.59	18.51
$Ru(CO)_2(N_2C_5Br_4)(PPh_3)_2\cdot CH_2Cl_2$ (VI)	yellow-orange	45.00	46.22	2.76	2.95	2.39	2.39	29.36	26.94
$Ru(CO)_2$(9-diazofluorene)$(PPh_3)_2\cdot CH_2Cl_2$ (VII)	red	65.14	66.39	4.21	4.27	2.92	2.73		
$Ru(CO)_2$(2,7-dibromo-9-diazofluorene)$(PPh_3)_2\cdot CH_2Cl_2$ (VIII)	orange	55.91	57.88	3.41	3.48	2.51	2.39	15.50	15.89

[a] Particularly in the Ru series the facile loss of initial CH_2Cl_2 of solvation from the crystalline samples makes the C analysis difficult.

Table II. Spectral Data for Diazo Complexes

compd	ν(NN), cm^{-1}	ν(CN) or ν(CO), cm^{-1}	^1H chem shift[a,f]	^{31}P chem shift[b,f]
$Ni(N_2C_5Cl_4)(t\text{-}BuNC)_2$ (I)	1557	2178, 2199	1.66 (*t*-Bu, s)[c,e]	
$Ni(N_2C_5Br_4)(t\text{-}BuNC)_2$ (II)	1541	2210, 2191	1.51 (*t*-Bu, s)[c,e]	
$Pt(N_2C_5Cl_4)(PPh_3)_2$ (III)	1496		7.32 (C_6H_5, m)[c]	18.78 (d), 12.28 (d)[c] ($^2J(PP) = 13.67$ Hz, $^1J(Pt\text{-}P_a) = 5232.7$ Hz, $^1J(Pt\text{-}P_b) = 4005.3$ Hz)
$Pt(N_2C_5Br_4)(PPh_3)_2$ (IV)	1490		7.20 (C_6H_5, m)[c]	13.79 (d), 10.89 (d)[d] ($^2J(PP) = 19.66$ Hz, $^1J(Pt\text{-}P_a) = 2897.6$ Hz, $^1J(Pt\text{-}P_b) = 3102.7$ Hz)
$Ru(CO)_2(N_2C_5Cl_4)(PPh_3)_2\cdot CH_2Cl_2$ (V)	1520	2021, 1961	7.36 (C_6H_5, m)[c]	34.09 (s)[c]
$Ru(CO)_2(N_2C_5Br_4)(PPh_3)_2\cdot CH_2Cl$ (VI)	1508	2023, 1951	7.34 (C_6H_5, m)[c]	33.62 (s)[c]
$Ru(CO)_2$(9-diazofluorene)$(PPh_8)_2\cdot CH_2Cl_2$ (VII)	1496	2002, 1931	7.10, 7.36 (C_6H_5, m)[c]	34.53 (s)[c]
$Ru(CO)_2$(2,7-dibromo-9-diazofluorene)$(PPh_3)_2\cdot CH_2Cl_2$ (VIII)	1495	2004, 1948	7.14, 7.38 (C_6H_5, m)[c]	34.53 (s)[c]

[a] Ppm downfield from external Me_4Si. [b] Ppm downfield from external H_3PO_4. [c] Spectrum obtained in $CDCl_3$ at −55 °C. [d] Spectrum obtained in CD_2Cl_2 at −85 °C. [e] Singlet to −90 °C. [f] s = singlet, d = doublet, m = multiplet.

compound $[Ru(CO)_2(N_2Ph)(PPh_3)_2][PF_6]$ was allowed to react with $NaBH_4$ for 3 h at room temperature to give 94% yield of $RuH_2(CO)_2(PPh_3)_2$. This ruthenium dihydride complex was then treated with a fourfold molar excess of PPh_3 in refluxing methanol for 3 h to give $Ru(CO)_2(PPh_3)_3$ in 91% yield. The tris(phosphine)ruthenium complex is easily converted to the ethylene complex by bubbling ethylene through a toluene suspension of $Ru(CO)_2(PPh_3)_3$ for 20–30 min followed by continued stirring under an ethylene atmosphere for several hours. Addition of ethylene-saturated hexane precipitates the ethylene complex in 98% yield.

Preparation of Nickel and Platinum Diazo Complexes. Bis(*tert*-butyl isocyanide)(tetrachlorodiazocyclopentadiene)nickel, $Ni(N_2C_5Cl_4)(t\text{-}BuNC)_2$ (I). An ether solution of "$Ni(t\text{-}BuNC)_2$" was allowed to react with an equimolar quantity of $N_2C_5Cl_4$ at −78 °C for 30–40 min, during which time the bright red color of the "$Ni(t\text{-}BuNC)_2$" species became dark green. Chilled hexane was added to complete the precipitation, and the yellow-green solid was collected at −78 °C, washed with diethyl ether, and dried in vacuo. The yield was 67%.

Bis(*tert*-butyl isocyanide)(tetrabromodiazocyclopentadiene)nickel, $Ni(N_2C_5Br_4)(t\text{-}BuNC)_2$ (II). This compound was prepared in the manner of I using $N_2C_5Br_4$ as the diazo ligand. The yield was 81% of dark green product.

Bis(triphenylphosphine)(tetrachlorodiazocyclopentadiene)platinum, $Pt(N_2C_5Cl_4)(PPh_3)_2$ (III). A dichloromethane solution of $Pt(C_2H_4)(PPh_3)_2$ was allowed to react with an equimolar quantity of $N_2C_5Cl_4$ at −78 °C for 30–40 min. Chilled hexane was added and the yellow solid was collected at −78 °C, washed with hexane, and dried in vacuo. The yield was 65%.

Bis(triphenylphosphine)(tetrabromodiazocyclopentadiene)platinum, $Pt(N_2C_5Br_4)(PPh_3)_2$ (IV). This compound was prepared exactly as was III using $N_2C_5Br_4$ as the diazo ligand. The yield was 75% of yellow solid.

Preparation of Ruthenium Diazo Complexes. Bis(triphenylphosphine)(tetrachlorodiazocyclopentadiene)dicarbonylruthenium, $Ru(CO)_2(N_2C_5Cl_4)(PPh_3)_2$ (V). A dichloromethane solution of $Ru(CO)_2(C_2H_4)(PPh_3)_2$ was allowed to react with an equimolar quantity of $N_2C_5Cl_4$ at 0 °C for 12 h Hexane was diffused into the solution over a period of days. The yield was 61% of a yellow-orange microcrystalline solid.

Bis(triphenylphosphine)(tetrabromodiazocyclopentadiene)dicarbonylruthenium, $Ru(CO)_2(N_2C_5Br_4)(PPh_3)_2$ (VI). This compound was prepared exactly as was V using $N_2C_5Br_4$ as the diazo ligand. The yield was 77% of yellow-orange microcrystalline solid.

Bis(triphenylphosphine)(9-diazofluorene)dicarbonylruthenium, $Ru(CO)_2(N_2C_{13}H_8)(PPh_3)_2$ (VII). This compound was prepared in the manner of V using 9-diazofluorene as the diazo molecule. The yield was 53% of bright red crystalline solid.

Bis(triphenylphosphine)(2,7-dibromo-9-diazofluorene)dicarbonylruthenium, $Ru(CO)_2(N_2C_{13}H_6Br_2)(PPh_3)_2$ (VIII). This compound was prepared by a similar procedure using 2,7-dibromo-9-diazofluorene as the diazo molecule. The yield was 50% of bright orange crystalline solid.

Thermolysis of "$Ni(N_2C_5Cl_4)(PPh_3)_2$" in the Presence of Diethyl Maleate—Attempted Synthesis of Cyclopropane Products. Attempts to isolate the nickel diazo complex $Ni(N_2C_5Cl_4)(PPh_3)_2$ were unsuccessful, and thus the complex was generated in situ by addition of the diazo ligand to a toluene solution of $Ni(C_2H_4)(PPh_3)_2$ at −78 °C. The yellow solution immediately became dark red. Excess diethyl maleate was added, and the solution was warmed to room temperature and then heated at 100 °C for 30 min. The black solution was evaporated in vacuo to give a black residue which was extracted with benzene and chromatographed on Fluorisil. The eluant consisted of unreacted diethyl maleate; no cyclopropane products were recovered.

Thermolysis of "$Ni(N_2C_5H_4)(PPh_3)_2$" in the Presence of Diethyl Maleate. The reaction sequence was analogous to the above using a stoichiometric quantity of $N_2C_5H_4$.[13] Chromatography on Florisil with benzene/acetone yielded a pale yellow solid, mp 233–236 °C. This material was identified as (triphenylphosphonium)cyclopentadienylidene, $Ph_3PC_5H_4$ (lit. mp 235–236 °C), by comparison[19] of the infrared spectrum. Anal. Calcd for $C_{23}H_{19}P$: C, 84.66; H, 5.83; N, 0; P, 9.50. Found: C, 82.28; H, 5.99; N, <0.1; P, 8.85. The yield was 6% on the basis of $N_2C_5H_4$.

Crystallographic Data for $Ru(CO)_2(N_2C_5Cl_4)(PPh_3)_2{\cdot}CH_2Cl_2$. Yellow-orange prisms suitable for X-ray diffraction studies were obtained as the CH_2Cl_2 solvate from a dichloromethane/*n*-hexane solution of V. Because the crystals easily lose dichloromethane of crystallization, freshly prepared crystals were mounted in capillaries in an atmosphere of the solvent to prevent desolvation while preliminary

---

(18) Cenini, S.; Porta, F.; Pizzotti, M. *Inorg. Chim. Acta* **1976**, *20*, 119–26.

(19) Lord, E.; Naan, M. P.; Hall, C. D. *J. Chem. Soc. B* **1970**, 1401–10.

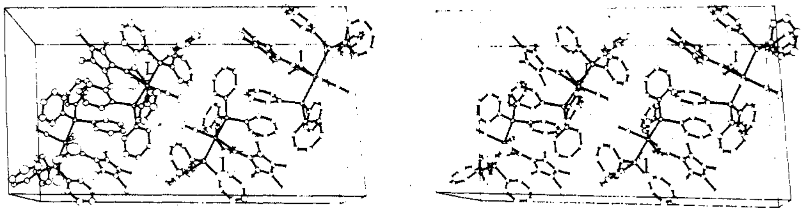


Figure 1. Stereoview of a unit cell of $Ru(CO)_2(N_2C_5Cl_4)(PPh_3)_2{\cdot}CH_2Cl_2$. The *x* axis is pointing toward the top of the page, the *y* axis is perpendicular to the paper pointing toward the reader, and the *z* axis is horizontal to the right. Vibrational ellipsoids are at the 20% probability level.

film data were obtained. The crystals show monoclinic symmetry and systematic extinctions ($0k0$, $k \neq 2n$; $h0l$, $l \neq 2n$) consistent with the space group C_{2h}^5-$P2_1/c$. Accurate cell dimensions (Table III) were determined by a least-squares analysis of the angular positions of 12 hand-centered reflections in diverse regions of reciprocal space (in the range $32° \geq 2\theta \geq 30°$).

Data collection was carried at −159 °C on a Picker four-circle diffractometer by using techniques standard in this laboratory.[20] A suitable crystal was mounted at −78 °C with Apiezon N grease on the end of a glass fiber and transferred directly into the N_2-cold stream. The intensities of 7903 reflections (all $\pm h$, $+k$, $+l$) were measured out to $2\theta = 48.4°$ by using Mo Kα radiation. Of the 7903 reflections measured, 7301 are unique, and of these 5728 have $F_o^2 > 3\sigma(F_o^2)$.

Solution and Refinement of the Structure of $Ru(CO)_2(N_2C_5Cl_4)(PPh_3){\cdot}CH_2Cl_2$. The coordination sphere about the ruthenium atom was readily located by using direct methods.[21] The usual procedure[20] for refinement was employed. Full-matrix least-squares refinements and difference Fourier syntheses were used to locate all remaining atoms. The function $\sum w(|F_o| - |F_c|)^2$ was minimized. Each phenyl group was treated throughout the refinement as a planar rigid body with uniform C–C distances of 1.395 Å and individual isotropic thermal parameters for each carbon atom. The ring carbon atoms of the diazo ligand were refined as individual atoms with anisotropic thermal parameters. All phenyl hydrogen-atom positions were idealized; the C–H distance was assumed to be 0.95 Å. The isotropic thermal parameter of a hydrogen atom was assumed to be 1.0 Å^2 larger than the thermal parameter of the carbon atom to which it is attached. All hydrogen atoms were included as fixed contributions in the final anisotropic refinements.

The final agreement indices, based on 5728 significant reflections and 262 variables, are $R = 0.057$ and $R_w = 0.065$. An analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, setting angles, and Miller indices shows no unusual trends other than slightly higher error values at lower 2θ values. This trend is perhaps indicative of an inadequate description of phenyl ring 6. High thermal parameters of 3.4–5.1 Å^2 of carbon atoms C(64), C(65), and C(66) (phenyl ring 6) are indicative of possible disorder in this ring; however our attempts to formulate a suitable disorder model were unsuccessful. The highest peak in the final difference Fourier map of 1.7 (1) e Å^3 is located near chlorine atom Cl(2) and is about 9% of the height of a typical chlorine atom in this structure. Peaks of slightly smaller density are also located near chlorine atoms Cl(3) and Cl(5).

The final positional and thermal parameters of atoms and groups appear in Tables IV and V, the idealized positions of the hydrogen atoms in Table VI,[22] and the root-mean-square amplitudes of vibration in Table VII.[22] A listing of the observed and calculated structure amplitudes is available.[22]

Results and Discussion

Table III. Summary of Crystal Data and Intensity Collection for $Ru(CO)_2(N_2C_5Cl_4)(PPh_3)_2{\cdot}CH_2Cl_2$

compd	$Ru(CO)_2(N_2C_5Cl_4)(PPh_3)_2{\cdot}CH_2Cl_2$
formula	$C_{44}H_{32}Cl_6N_2O_2P_2Ru$
fw	996.49
a	14.66 (1) Å
b	10.891 (7) Å
c	26.73 (2) Å
β	94.11 (2)°
V	4257 Å^3
Z	4
d (calcd)	1.554 g/cm^3 (−159 °C)[a]
d (obsd)	1.48 (4) g/cm^3 (25 °C)
space group	C_{2h}^5-$P2_1/c$
cryst dimens	0.13 × 0.33 × 0.82 mm; 0.017 mm^3
cryst shape	prism with bounding planes {100}, {011}, $\{10\bar{1}\}$
temp	−159 °C
radiation	Mo Kα (λ(Mo Kα_1) = 0.709 30 Å)
μ (Mo Kα)	8.54 cm^{-1}
transmission factors	0.68–0.90
receiving aperature	4.8 mm wide × 5.2 mm high; 33 cm from the crystal
takeoff angle	3.4°
scan speed	2.0° in 2θ/min
scan range	$2\theta < 20°$, 0.8° below Kα_1 to 0.75° above Kα_2; $2\theta > 20°$, 1.0° below Kα_1 to 0.75° above Kα_2
bkgd counting time, total	20 s with rescan option[b]
2θ limits	3.3–48.4°
p	0.04
unique data $F_o^2 > 3\sigma(F_o^2)$	5728
final no. variables	262
error in observn of unit wt	2.21 e
R	0.057
R_w	0.065

[a] The low-temperature system is based on a design by J. C. Huffman (Ph.D. Thesis, Indiana University, 1974). [b] The diffractometer was run under the Vanderbilt disk oriented system (Lenhert, P. G. *J. Appl. Crystallogr.* 1975, *8*, 568–70).

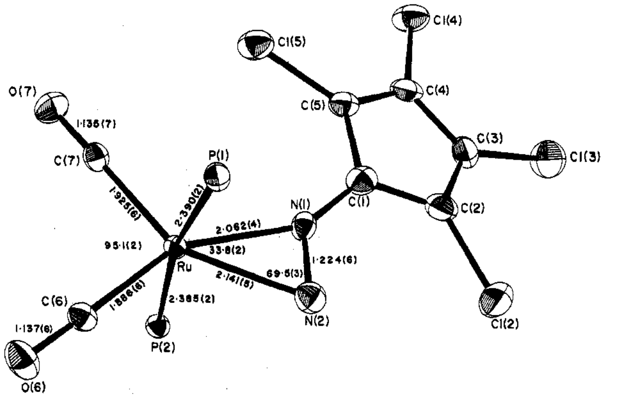


Figure 2. Coordination sphere with some bond distances and angles for $Ru(CO)_2(N_2C_5Cl_4)(PPh_3)_2$. Vibrational ellipsoids are drawn at the 50% probability level.

Structure of $Ru(CO)_2(N_2C_5Cl_4)(PPh_3)_2{\cdot}CH_2Cl_2$. Compound V, $Ru(CO)_2(N_2C_5Cl_4)(PPh_3)_2$, was prepared by the reaction of $N_2C_5Cl_4$ with $Ru(CO)_2(C_2H_4)(PPh_3)_2$ in CH_2Cl_2. Crystals of the CH_2Cl_2 solvate, suitable for diffraction study, were obtained from CH_2Cl_2/hexane. The crystal structure consists

---

(20) See, for example: Waters, J. M.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3273–7.

(21) The MULTAN 78 package of Main was used. Other programs for the CDC 6600 computer include the Northwestern absorption program AGNOST and local modifications of Zalkin's FORDAP Fourier program, Johnson's ORTEP II thermal ellipsoid plotting program, and Busing and Levy's ORFFE error function program. Our full-matrix, least-squares program NUCLS, in its nongroup form, closely resembles the Busing–Levy ORFLS program.

(22) Supplementary material.

Table IV. Positional and Thermal Parameters for the Nongroup Atoms of $Ru(CO)_2(N_2C_5Cl_4)(P(C_6H_5)_3)_2 \cdot CH_2Cl_2$

ATOM	X[A]	Y	Z	B11[B]	B22	B33	B12	B13	B23
RU	0.359215(29)	0.095465(41)	0.100215(15)	14.59(22)	22.01(40)	3.42(6)	0.39(26)	0.67(8)	0.26(13)
P(1)	0.489613(94)	0.19498(13)	0.140831(49)	15.87(67)	24.0(13)	3.99(19)	-0.04(77)	1.35(28)	-0.53(40)
P(2)	0.217941(96)	0.03589(13)	0.057231(50)	16.84(69)	27.3(13)	4.22(20)	-0.47(80)	-0.02(29)	-0.38(42)
CL(2)	0.14013(11)	0.33945(16)	0.206379(59)	43.93(92)	51.8(16)	10.69(25)	17.9(10)	5.51(38)	1.29(52)
CL(3)	0.06731(12)	0.17615(18)	0.303381(60)	42.34(94)	102.6(21)	9.09(25)	24.4(12)	8.62(38)	1.62(58)
CL(4)	0.18028(10)	-0.09195(16)	0.312836(55)	29.37(77)	68.8(16)	8.44(22)	8.0(10)	2.24(33)	10.06(52)
CL(5)	0.33278(10)	-0.09882(15)	0.222071(53)	27.62(75)	54.2(15)	8.34(22)	4.75(93)	2.33(32)	7.25(49)
CL(6)	-0.10127(18)	0.06096(26)	0.39259(10)	71.6(16)	150.6(33)	30.23(55)	-30.0(19)	3.29(75)	-21.5(11)
CL(7)	-0.27105(21)	0.12057(23)	0.33606(12)	100.5(20)	77.9(26)	39.98(68)	7.2(18)	-4.72(92)	-0.1(10)
N(1)	0.28623(29)	0.15048(44)	0.15943(16)	13.2(22)	31.4(44)	6.03(68)	2.3(27)	0.35(97)	-1.8(15)
N(2)	0.28161(31)	0.23949(47)	0.13140(17)	22.5(25)	42.4(50)	6.97(73)	0.5(30)	-0.2(11)	-2.4(16)
C(1)	0.24844(38)	0.12815(54)	0.20403(21)	18.1(28)	40.2(58)	7.54(89)	0.1(33)	-1.5(13)	-1.0(18)
C(2)	0.18162(40)	0.19878(57)	0.22656(21)	30.6(32)	44.9(59)	5.53(85)	0.1(37)	-3.1(13)	0.6(18)
C(3)	0.15242(41)	0.13398(59)	0.26574(21)	28.1(32)	60.1(64)	5.28(86)	7.1(38)	0.8(13)	-4.6(19)
C(4)	0.20032(40)	0.02194(55)	0.27018(20)	30.3(32)	39.4(59)	5.34(83)	-0.4(36)	-3.9(13)	2.9(18)
C(5)	0.25918(38)	0.01812(53)	0.23312(20)	23.5(30)	34.0(56)	5.94(84)	-2.1(33)	-1.2(12)	2.4(17)
C(6)	0.40895(37)	0.12501(49)	0.03818(20)	19.7(28)	28.3(54)	4.37(80)	-4.7(31)	-0.8(12)	-0.7(16)
O(6)	0.44079(28)	0.14031(38)	0.00119(14)	38.4(23)	48.8(42)	5.42(61)	-10.3(26)	5.55(96)	0.3(13)
C(7)	0.40334(37)	-0.07071(53)	0.10657(19)	18.0(27)	33.9(58)	4.55(78)	-2.2(33)	2.1(11)	-0.5(16)
O(7)	0.42648(28)	-0.17006(39)	0.10980(15)	32.5(24)	34.4(43)	9.34(67)	7.5(26)	1.32(96)	2.6(13)
C(8)	-0.21837(57)	0.04058(85)	0.38743(37)	50.6(50)	107.(10)	37.8(21)	-19.0(59)	18.0(26)	23.5(38)

[A] ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. [B] THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: $EXP[-(B11H^2+B22K^2+B33L^2+2B12HK+2B13HL+2B23KL)]$. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS X 10^4.

Table V. Derived Parameters for the Rigid-Group Atoms of $Ru(CO)_2(N_2C_5Cl_4)(P(C_6H_5)_3)_2 \cdot CH_2Cl_2$

ATOM	X	Y	Z	B, A^2	ATOM	X	Y	Z	B, A^2
C(11)	0.47175(24)	0.22677(32)	0.205598(91)	1.36(10)	C(41)	0.21455(24)	-0.10806(29)	0.02227(13)	1.52(10)
C(12)	0.49515(24)	0.13812(28)	0.24195(12)	1.72(10)	C(42)	0.13318(19)	-0.17363(36)	0.01378(14)	2.26(11)
C(13)	0.46746(26)	0.15186(30)	0.29049(11)	1.98(11)	C(43)	0.12992(21)	-0.27635(35)	-0.01748(15)	2.80(13)
C(14)	0.41636(26)	0.25425(34)	0.302679(93)	2.13(11)	C(44)	0.20804(27)	-0.31349(31)	-0.04026(14)	2.77(13)
C(15)	0.39296(25)	0.34291(29)	0.26633(12)	1.96(11)	C(45)	0.28941(21)	-0.24792(36)	-0.03177(14)	2.76(12)
C(16)	0.42065(25)	0.32917(28)	0.21779(11)	1.57(10)	C(46)	0.29266(19)	-0.14521(34)	-0.00051(14)	1.89(10)
C(21)	-0.40072(18)	0.11482(30)	0.14225(12)	1.76(9)	C(51)	0.12765(23)	0.02165(34)	0.09944(12)	1.58(10)
C(22)	-0.33054(22)	0.14221(30)	0.17855(11)	1.65(10)	C(52)	0.05935(26)	0.11007(31)	0.10218(13)	2.44(12)
C(23)	-0.24816(19)	0.07787(35)	0.17952(12)	2.07(11)	C(53)	-0.00162(24)	0.10312(35)	0.13982(15)	3.13(13)
C(24)	-0.23597(18)	-0.01387(33)	0.14418(13)	2.00(11)	C(54)	0.00571(25)	0.00775(40)	0.17472(13)	3.03(13)
C(25)	-0.30615(23)	-0.04126(29)	0.10788(12)	1.80(10)	C(55)	0.07401(27)	-0.08067(33)	0.17198(13)	2.55(12)
C(26)	-0.38852(19)	0.02308(32)	0.10691(11)	1.39(10)	C(56)	0.13498(23)	-0.07372(31)	0.13434(14)	2.07(11)
C(31)	-0.48702(24)	0.34634(27)	0.11376(13)	1.49(10)	C(61)	0.17595(26)	0.14907(33)	0.01074(12)	1.55(10)
C(32)	-0.40229(20)	0.40243(33)	0.12431(13)	1.94(10)	C(62)	0.12263(26)	0.11592(27)	-0.03247(13)	1.91(11)
C(33)	-0.38457(20)	0.51693(34)	0.10371(14)	2.38(12)	C(63)	0.09363(25)	0.20533(36)	-0.06745(11)	2.01(11)
C(34)	-0.45160(26)	0.57535(28)	0.07256(14)	2.54(12)	C(64)	0.11795(30)	0.32789(32)	-0.05922(15)	3.40(14)
C(35)	-0.53634(23)	0.51926(35)	0.06202(14)	3.01(13)	C(65)	0.17128(33)	0.36105(28)	-0.01601(17)	5.07(19)
C(36)	-0.55405(19)	0.40476(35)	0.08262(14)	2.36(11)	C(66)	0.20028(28)	0.27164(38)	0.01897(13)	3.96(16)

RIGID GROUP PARAMETERS

GROUP	X_C[A]	Y_C	Z_C	DELTA[B]	EPSILON	ETA
RING 1	0.44406(16)	0.24051(23)	0.254139(84)	0.4824(23)	2.9045(17)	-1.3618(24)
RING2	-0.31634(15)	0.05048(22)	0.143215(81)	2.5626(27)	2.2672(23)	0.0679(30)
RING3	-0.46931(17)	0.46084(24)	0.093162(87)	1.5594(23)	2.7354(23)	2.6814(25)
RING4	0.21129(17)	-0.21078(24)	-0.008994(88)	-1.4389(23)	2.9121(23)	2.4823(25)
RING5	0.06668(17)	0.01470(25)	0.137084(93)	-2.6368(25)	-2.8129(22)	-2.1966(26)
RING6	0.14695(17)	0.23848(26)	-0.02424(10)	-0.5900(29)	-2.5768(23)	0.8750(28)

[A] X_C, Y_C, AND Z_C ARE THE FRACTIONAL COORDINATES OF THE ORIGIN OF THE RIGID GROUP. [B] THE RIGID GROUP ORIENTATION ANGLES DELTA, EPSILON, AND ETA(RADIANS) HAVE BEEN DEFINED PREVIOUSLY: S.J. LA PLACA AND J.A. IBERS, ACTA CRYSTALLOGR., 18, 511(1965).

of the packing of four molecules of the ruthenium complex and four dichloromethane molecules in the unit cell. A stereo drawing of the unit cell is shown in Figure 1. There are no significant intermolecular contacts, the shortest being N(2)–H1C(8) = 2.43 Å, H1C(12)–H1C(15) = 2.37 Å, and H1C(66)–H1C(8) = 2.53 Å. The labeling scheme for this complex, together with some bond distances and angles, is shown in Figures 2 and 3.

The diazo ligand is coordinated to the ruthenium atom in the η^2 fashion through the N–N multiple bond. The Ru–N distances are essentially equal. If the diazo ligand is assumed to occupy one coordination site, then there is approximate trigonal-bipyramidal geometry about the ruthenium atom with trans apical phosphines (P(1)–Ru–P(2) = 168.80 (5)°) and with the two carbonyl ligands and the diazo ligand occupying the trigonal plane. The Ru, C(6), O(6), C(7), O(7), N(1), and N(2) atoms lie in a plane; the distances of these atoms from the least-squares plane (plane 1) are 0.0009 (4), −0.017 (5), −0.007 (4), 0.011 (5), −0.027 (4), 0.008 (4), and −0.054 (5) Å, respectively. The nine atoms of the tetrachlorocyclo-

Table VIII. Selected Distances (Å) and Angles (Deg) in $Ru(CO)_2(N_2C_5Cl_4)(P(C_6H_5)_3)_2 \cdot CH_2Cl_2$

			Bond Distances		
Ru-P(1)	2.390 (2)		C(1)-C(2)	1.414 (8)	1.394 (34)
Ru-P(2)	2.385 (2)		C(1)-C(5)	1.431 (8)	
Ru-C(6)	1.886 (6)		C(2)-C(3)	1.357 (8)	
Ru-C(7)	1.925 (6)		C(3)-C(4)	1.409 (8)	
Ru-N(1)	2.062 (4)		C(4)-C(5)	1.360 (8)	
Ru-N(2)	2.141 (5)		P(1)-C(11)	1.803 (3)	1.822 (14)
N(1)-N(2)	1.224 (6)		P(1)-C(21)	1.828 (3)	
N(1)-C(1)	1.372 (7)		P(1)-C(31)	1.842 (4)	
C(2)-Cl(2)	1.721 (6)	1.718 (8)[a]	P(2)-C(41)	1.824 (4)	
C(3)-Cl(3)	1.720 (6)		P(2)-C(51)	1.807 (4)	
C(4)-Cl(4)	1.724 (6)		P(2)-C(61)	1.826 (4)	
C(5)-Cl(5)	1.709 (6)		C(8)-Cl(6)[b]	1.727 (8)	
C(6)-O(6)	1.137 (6)		C(8)-Cl(7)	1.759 (10)	
C(7)-O(7)	1.135 (7)				
			Bond Angles		
C(6)-Ru-C(7)	95.1 (2)		Cl(2)-C(2)-C(1)	126.2 (5)	125.7 (10)
C(6)-Ru-N(1)	151.6 (2)		Cl(2)-C(2)-C(3)	125.5 (5)	
C(6)-Ru-N(2)	117.8 (2)		Cl(3)-C(3)-C(2)	126.5 (5)	
C(6)-Ru-P(2)	90.0 (2)		Cl(3)-C(3)-C(4)	124.1 (5)	
C(6)-Ru-P(1)	88.6 (2)		Cl(4)-C(4)-C(3)	124.8 (5)	
C(7)-Ru-N(1)	113.3 (2)		Cl(4)-C(4)-C(5)	127.3 (5)	
C(7)-Ru-N(2)	147.0 (2)		Cl(5)-C(5)-C(1)	125.2 (4)	
C(7)-Ru-P(1)	97.7 (2)		Cl(5)-C(5)-C(4)	126.2 (5)	
C(7)-Ru-P(2)	93.5 (2)		C(2)-C(1)-C(5)	106.1 (5)	108.0 (12)
N(1)-Ru-N(2)	33.8 (2)		C(3)-C(2)-C(1)	108.2 (5)	
N(1)-Ru-P(2)	88.2 (1)		C(2)-C(3)-C(4)	109.4 (5)	
N(1)-Ru-P(1)	87.8 (1)		C(3)-C(4)-C(5)	107.7 (5)	
N(2)-Ru-P(2)	85.4 (1)		C(4)-C(5)-C(1)	108.6 (5)	
N(2)-Ru-P(1)	85.5 (1)		C(31)-P(1)-C(21)	104.3 (2)	104.5 (5)
P(2)-Ru-P(1)	168.80 (5)		C(11)-P(1)-C(31)	104.4 (2)	
N(2)-N(1)-C(1)	131.6 (5)		C(11)-P(1)-C(21)	105.1 (2)	
N(2)-N(1)-Ru	76.7 (3)		C(51)-P(2)-C(41)	104.6 (2)	
C(1)-N(1)-Ru	151.6 (4)		C(51)-P(2)-C(61)	104.9 (2)	
N(1)-N(2)-Ru	69.5 (3)		C(41)-P(2)-C(61)	103.7 (2)	
O(6)-C(6)-Ru	178.2 (5)		Ru-P(1)-C(11)	110.9 (1)	114.1 (31)
O(7)-C(7)-Ru	177.7 (5)		Ru-P(1)-C(21)	117.8 (1)	
Cl(6)-C(8)-Cl(7)	112.1 (4)		Ru-P(1)-C(31)	113.1 (1)	
			Ru-P(2)-C(41)	118.1 (1)	
			Ru-P(2)-C(51)	111.9 (1)	
			Ru-P(2)-C(61)	112.5 (1)	

[a] The figure in parentheses following an average value is the larger of that estimated for an individual value from the inverse matrix or on the assumption that the values averaged are from the same population. [b] The atoms of the CH_2Cl_2 solvent are C(8), Cl(6), and Cl(7).

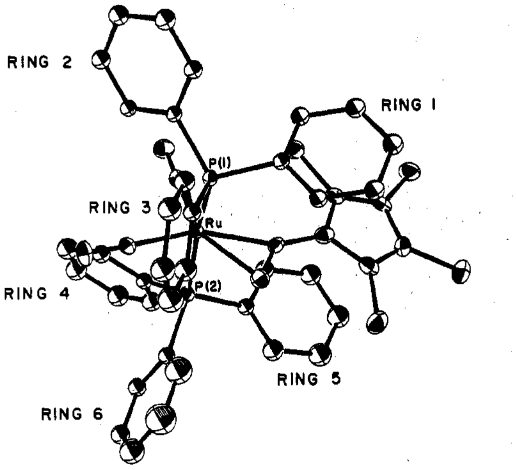


Figure 3. Drawing of an individual molecule of $Ru(CO)_2(N_2C_5Cl_4)(PPh_3)_2$. Vibrational ellipsoids are drawn at the 50% probability level. The H atoms have been omitted for the sake of clarity.

pentadiene fragment, C(1), C(2), C(3), C(4), C(5), Cl(2), Cl(3), Cl(4), and Cl(5), all lie in a plane; the deviations of these atoms from the least-squares plane (plane 2) are −0.011 (6), 0.031 (6), 0.051 (6), 0.050 (6), 0.023 (5), −0.015 (2), 0.017 (2), −0.019 (2), and 0.006 (2) Å, respectively. The dinitrogen portion of the diazo ligand does not lie in the plane with the $-C_5Cl_4$ fragment; the N(1) and N(2) atoms lie −0.23 and −0.29 Å, respectively, from plane 2. The dihedral angle between plane 1 and plane 2 is 13.5°. In the other known example of η^2 coordination of an N_2R molecule, namely, in Ni(*t*-BuNC)$_2$(diazofluorene),[1b] the diazofluorene moiety is planar and makes an angle of 5.9 (2)° with the NiC_2 plane.

The metal–ligand distances (Table VIII) are normal. Thus the Ru–P distances of 2.388 (2) Å in $Ru(CO)_2(N_2C_5Cl_4)(PPh_3)_2$ are very similar to those of five- and six-coordinate Ru(0) and Ru(II) complexes with trans phosphine ligands (see Table IX). The Ru–C (of CO) distances of 1.925 (6) and 1.886 (6) Å in the present complex may be compared with those of 1.911 (8) and 1.912 (7) Å in $[Ru(Cl(CO)_2(HNNPh)(PPh_3)_2][ClO_4]$[23] and those of 1.908 (8) and 1.924 (6) Å in $Ru(CO)_3(COT)$.[24] The C–O distances of 1.135 (7) and 1.137 (6) Å in the present complex are normal. The diazo molecule is asymmetrically bonded to the Ru atom as shown by the significantly different Ru–N distances (2.062 (4), 2.141 (5) Å). This asymmetry is further reflected in the Ru–C (of CO) distances (1.925 (6), 1.886 (6) Å).

Comparisons of the geometry of the bound $N_2C_5Cl_4$ molecule are limited as the structure of the free molecule is unknown and the present structure is the first to be reported in

---

(23) Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 5369–79.
(24) Cotton, F. A.; Eiss, R. *J. Am. Chem. Soc.* **1969**, *91*, 6593–7.

Table IX. Comparison of Trans Ru-P Bond Distances in Five- and Six-Coordinate Ru(0) and Ru(II) Complexes

compd	Ru-P(1), Å	Ru-P(2), Å	P(1)-Ru-P(2), deg
$[RuCl(NO)_2(PPh_3)_2][PF_6]$[a]	2.432 (5)	2.424 (5)	159.6 (2)
$RuHCl(PPh_3)_3$[b]	2.361 (4)	2.329 (4)	153.1 (2)
$RuCl_2(PPh_3)_3$[c]	2.374 (6)	2.412 (6)	156.4 (2)
$RuCl_3(NO)(PMePh_2)_2$[d]	2.441 (2)	2.429 (2)	171.46 (6)
$RuCl_3(NO)(PPh_3)_2$[e]	2.465 (1)	2.465 (1)	177.49 (8)
$RuCl_3(NNC_6H_4CH_3)(PPh_3)_2$[e]	2.436 (2)	2.437 (2)	173.56 (6)
$[RuCl(CO)_2(NHNPh)(PPh_3)_2][ClO_4]$[f]	2.439 (2)	2.415 (2)	176.83 (5)
$RuCl(NO)(\eta^2\text{-}SO_2)(PPh_3)_2$[g]	2.433 (2)	2.430 (2)	172.09 (6)
$Ru(CO)_2(N_2C_5Cl_4)(PPh_3)_2\cdot CH_2Cl_2$[h]	2.390 (2)	2.385 (2)	168.80 (5)

[a] Pierpont, C. G.; Van Derveer, D. G.; Durland, W.; Eisenberg, R. *J. Am. Chem. Soc.* 1970, *92*, 4760-2. [b] Skapski, A. C.; Troughton, P. G. H. *Chem. Commun.* 1968, 1230-1. [c] La Placa, S. J.; Ibers, J. A. *Inorg. Chem.* 1965, *4*, 778-83. [d] Schultz, A. J.; Henry, R. L.; Reed, J.; Eisenberg, R. *Ibid.* 1974, *13*, 732-6. [e] Haymore, B. L.; Ibers, J. A. *Ibid.* 1975, *14*, 3060-70. [f] Reference 23. [g] Wilson, R. D.; Ibers, J. A. *Inorg. Chem.* 1978, *17*, 2134-8. [h] This work.

Table X. Carbonyl Stretching Frequencies for Some $Ru(CO)_2(PPh_3)_2(AB)$ Complexes

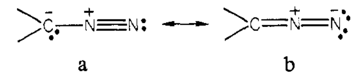
AB	ν(CO), cm^{-1}	AB	ν(CO), cm^{-1}
CO	1900[a]	O_2	2005, 1945[b]
PhCCPh	1950, 1895[b]	H_2	2015, 1970[d]
C_2H_4	1955, 1900[b]	$N_2C_5Cl_4$	2021, 1961[c]
9-diazofluorene	2002, 1931[c]	$N_2C_5Br_4$	2023, 1951[c]
2,7-dibromo-9-diazofluorene	2004, 1948[c]		

[a] Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* 1974, *15*, 50-1. [b] Reference 17. [c] This work. [d] Reference 18.

which the molecule is η^2 coordinated. The N(1)-N(2) distance of 1.224 (6) Å corresponds to a slightly shortened N-N double bond when compared with the distances observed in HN=NH,[25] $CH_3N{=}NCH_3$,[26] and PhN=NPh[27] (1.238 (7), 1.254 (3), and 1.244 Å, respectively). However, the N(1)-N(2) bond length is comparable with that reported for $Ni(t\text{-}BuNC)_2$(diazofluorene)[1b] (1.245 (4) Å). The N(1)-C(1) distance of 1.372 (7) Å is intermediate between a N-C single and double bond; this value is comparable with that of 1.347 (9) Å reported for the η^1-bound $N_2C_5Cl_4$ molecule in $IrCl(N_2C_5Cl_4)(PPh_3)_2$.[7] The bond angles of the Ru-N(2)-N(1)-C(1) fragment are very similar to those reported respectively for the Ni-N(2)-N(1)-C(1) fragment of $Ni(t\text{-}BuNC)_2$(diazofluorene):[1b] M-N(2)-N(1) = 69.5 (3), 68.7 (2)°; M-N(1)-N(2) = 76.7 (3), 72.1 (2)°; N(1)-M-N(2) = 33.8 (2), 39.2 (1)°; N(2)-N(1)-C(1) = 131.6 (5), 133.8 (3)°. The bond distances in the C_5Cl_4 ring are also similar to those in $IrCl(N_2C_5Cl_4)(PPh_3)_2$;[7] however the diene nature of the cyclopentadienyl ring is more pronounced, namely, two short (1.357 (8), 1.360 (8) Å) and three long (1.414 (8), 1.431 (8), 1.409 (8) Å) carbon-carbon bonds. This asymmetry in the ring is not as great as in $Mn(CO)_5(\eta^1\text{-}C_5Cl_5)$[28] (1.356 (8), 1.345 (8), 1.487 (8), 1.499 (8), 1.474 (8) Å).

Discussion of the Bonding. The η^2 coordination of the $N_2C_5Cl_4$ ligand to the Ru center we ascribe to a π interaction through the N-N multiple bond. A similar description has been applied to the diazo molecule in $Ni(t\text{-}BuNC)_2$(diazofluorene).[1b] On the basis of spectroscopic observations, this bonding mode has been assigned to the analogous palladium systems PdL_2(diazofluorene) (L = t-BuNC, PPh_3) as well as to other diazoalkane nickel systems NiL_2(diphenyldiazomethane) (L = t-BuNC, PPh_3)[1a] and to $Mo(C_5H_5)_2$(diazofluorene).[29] Presumably the metal atoms in these complexes are too electron rich to function as σ-electron acceptors and prefer instead to be electron donors, with the diazo molecules functioning as π acids. Similarly the Ru center in the π complexes reported here is also behaving as a strong electron donor. Such behavior has been previously observed for Ru(0) in $Ru(CO)_2(C_2H_4)(PPh_3)_2$[17] and $Ru(CO)_2(PhCCPh)(PPh_3)_2$.[17]

In the present complex the coordination of the $N_2C_5Cl_4$ moiety to Ru such that the $(OC)_2RuN_2C_5Cl_4$ fragment is approximately planar (dihedral angle 13.5°) is not unexpected; a consideration of the molecular orbitals of the closely related diazomethane molecule indicates that the lowest unoccupied molecular orbital (LUMO) is on the two nitrogen atoms in the molecular plane,[30] this being the π-acceptor orbital of diazomethane. Indeed, the diazofluorene molecule also utilizes the molecular orbitals in the plane of the molecule when coordinated to the "$Ni(t\text{-}BuNC)_2$" fragment.[1b] The observed inequality of the Ru-N bond distances is consistent with the inequality of the Ni-N bonds (1.874 (3), 1.834 (3) Å) in $Ni(t\text{-}BuNC)_2$(diazofluorene).[1b] Presumably the observed difference in the Ru-N distances reflects the stronger π acidity of atom N(1) compared with atom N(2). This is reasonable, on the basis of the two most likely contributing valence-bond formulations for the free diazo molecule.



a b

In both cases the inner nitrogen atom (N(1)) is electron poor, whereas the outer nitrogen atom (N(2)) is electron rich. We would expect atom N(1) to be the better electron acceptor and that the electron-withdrawing properties of the $-C_5Cl_4$ fragment would further enhance the π acidity of atom N(1). Both these effects would result in a shorter Ru-N(1) distance as observed. If we accept the covalent radii of ruthenium and nitrogen as 1.33 and 0.92 Å, respectively,[31] then both Ru-N distances are significantly shorter than that expected for a Ru-N single bond, consistent with the proposed π-accepting properties of the $N_2C_5Cl_4$ molecule. The observed inequality of the Ni-N bonds of $Ni(t\text{-}BuNC)_2$(diazofluorene)[1b] has also been explained in terms of the better electron-accepting ability of the inner nitrogen atom of the diazofluorene group.

π Acidity of Diazo Ligands. A sensitive indication of the relative π acidities of π ligands, AB, in $Ni(t\text{-}BuNC)_2(AB)$ complexes is the CN stretching frequency of the t-BuNC ligands.[32,33] As the π acidity of AB increases, less electron density is available for π back-bonding onto the t-BuNC ligands, with concomitant lengthening of the Ni-C distances (of the t-BuNC ligands) and contraction of the C≡N distances. This results in a higher value of ν(CN). An extensive compilation of CN stretching frequencies for a number of π-acid-Ni systems has been reported;[33] values of ν(CN) of about 2000 cm^{-1} correspond formally to Ni(0) systems ($Ni(t\text{-}BuNC)_4$, ν(CN) = 2000 cm^{-1}), whereas values near 2200 cm^{-1} correspond to Ni(II) ($Ni(O_2)(t\text{-}BuNC)_2$, ν(CN) = 2196, 2178

---

(25) Trombetti, A. *Can. J. Phys.* **1968**, *46*, 1005-11.

(26) Chang, C. H.; Porter, R. F.; Bauer, S. H. *J. Am. Chem. Soc.* **1970**, *92*, 5313-8.

(27) Brown, C. J. *Acta Crystallogr.* **1966**, *21*, 153-8.

(28) Day, V. W.; Stults, B. R.; Reimer, K. J.; Shaver, A. *J. Am. Chem. Soc.* **1974**, 96, 4008-9.

(29) Nakamura, A.; Aotake, M.; Otsuka, S. *J. Am. Chem. Soc.* **1974**, *96*, 3456-62.

(30) Jorgensen, W. L.; Salem, L. "The Organic Chemist's Book of Orbitals"; Academic Press: New York, 1973.

(31) Jesson, J. P.; Muetterties, E. L. "Chemists Guide to Basic Chemical and Physical Data"; Marcel Dekker: New York, 1969.

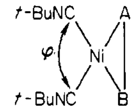
(32) Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33-61.

(33) Ittel, S. D. *Inorg. Chem.* **1977**, *16*, 2589-97.

cm^{-1}). This indicates the importance of π bonding in stabilizing these complexes. Comparison of the values of ν(CN) for the neutral diazo complexes (Ni(N_2R)(*t*-BuNC)$_2$ [R = C_5Cl_4, ν = 2199, 2178 cm^{-1}; *R* = C_5Br_4, ν = 2210, 2191 cm^{-1}] with those of the O_2 (ν = 2196, 2178 cm^{-1}) and tetracyanoethylene (ν = 2194, 2179 cm^{-1}) complexes suggests that the diazocyclopentadiene systems are perhaps best described as those of Ni(II).

In an analogous manner, the CO stretching frequencies of Ru(CO)$_2$(PPh$_3$)$_2$(AB) complexes should be a sensitive probe of the relative π acidities of AB on the ruthenium center. A tabulation of ν(CO) values for a number of complexes is given in Table X. Higher values of ν(CO) (~2000 cm^{-1}) correspond formally to Ru(II) species (e.g., RuH$_2$(CO)$_2$(PPh$_3$)$_2$ with ν = 2105, 1970 cm^{-1}),[18] while lower values of ν(CO) (~1900 cm^{-1}) correspond to Ru(0) (e.g., Ru(CO)$_3$(PPh$_3$)$_2$[34] with ν = 1900 cm^{-1}). The trend in CO stretching frequencies for these complexes parallels that for the CN stretching frequencies in the Ni complexes. Again the substituted diazocyclopentadiene molecules are comparable with O_2 in their electron-accepting ability.

A comparison of the metrical details of the Ni(*t*-BuNC)$_2$(AB) complexes with the CN stretching frequencies produced a very interesting trend.[1b] With the exception of *t*-BuN=C=C(CN)$_2$, all complexes show a decrease in the angle φ from 106.3 (16)° for AB = PhCCPh[35] to 91.8 (5)° for AB = O_2.[36] Corresponding to this decrease in φ there is an increase in the CN stretching frequency and therefore in the π acidity of AB. We anticipate that the value of φ for the Ni($N_2C_5Cl_4$)(*t*-BuNC)$_2$ and Ni($N_2C_5Br_4$)(*t*-BuNC)$_2$ complexes should be around the O_2 value of 92°. Furthermore, we expect that the φ angle (OC–Ru–CO) in the Ru(CO)$_2$(PPh$_3$)$_2$(AB) complexes should be strongly correlated with the CO stretching frequencies and thus with the π acidity of AB. It is interesting that the C(6)–Ru–C(7) angle (φ) of 95.1 (2)° in the present structure deviates significantly from 120° and is comparable with those found in the Ni systems. This suggests that the same factors which cause a decrease in the φ angle for the nickel species hold for the ruthenium complex. The correlation of φ with CN stretching frequencies in Ni(*t*-BuNC)$_2$(AB) species has been interpreted[1b] in terms of repulsion between the bonding electron pairs. With increasing π acidity of AB, less electron density is back-donated into the *t*-BuNC ligands. This results in less repulsion between the bonding orbitals of these ligands and hence a decrease in the value of φ.

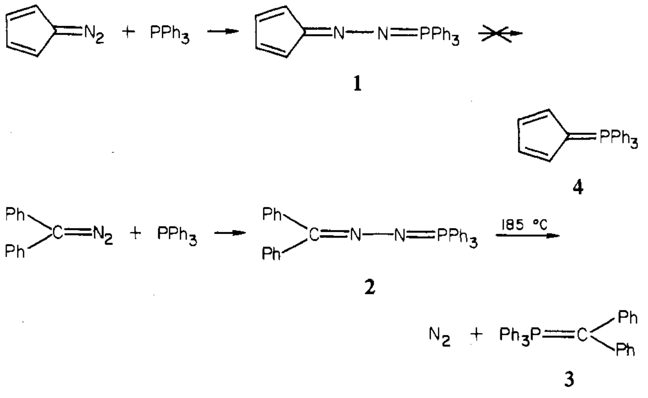


Synthesis of Diazo Complexes of Ni(0), Pt(0), and Ru(0). A series of ruthenium diazo complexes Ru(CO)$_2$(N_2R)(PPh$_3$)$_2$ (N_2R = $N_2C_5Cl_4$, $N_2C_5Br_4$, 9-diazofluorene, 2,7-dibromo-9-diazofluorene) have been prepared by the reaction of the given diazo molecule with Ru(CO)$_2$(C_2H_4)(PPh$_3$)$_2$ (see Table II). These complexes are the first in which neutral diazo molecules are coordinated to a ruthenium center. These ruthenium complexes exhibit similar, low NN stretching frequencies in the infrared region (1495, 1496, 1508, 1520 cm^{-1}). On the basis of the close correspondence in stretching frequencies and the known structure of the $N_2C_5Cl_4$ complex, we believe that all four complexes have the N_2R molecule bound to the Ru center in the η^2 manner.

The nickel diazo complexes NiL(*t*-BuNC)$_2$ (L = $N_2C_5Cl_4$, $N_2C_5Br_4$) have been prepared by the low-temperature reaction of "Ni(*t*-BuNC)$_2$" with the given diazo molecule. These complexes are unstable in solution above −50 °C and decompose slowly in the solid state. They exhibit strong infrared bands at 2178, 2199 ($N_2C_5Cl_4$) and 2210, 2191 cm^{-1} ($N_2C_5Br_4$) which we assign to ν(CN) of the *t*-BuNC ligands. Medium intensity infrared bands occur at 1557 ($N_2C_5Cl_4$) and 1541 cm^{-1} ($N_2C_5Br_4$) cm^{-1} which we attribute to ν(NN). Both the NN and CN stretching frequencies are higher for these complexes than for the analogous diazofluorene complex (ν(CN) = 2180, 2158; ν(NN) = 1509 cm^{-1}); however, the general correspondence of NN stretching frequencies suggests that the $N_2C_5Cl_4$ and $N_2C_5Br_4$ molecules are also π bonded in the nickel systems.

The substituted diazocyclopentadiene complexes PtL(PPh$_3$)$_2$ (L = $N_2C_5Cl_4$, $N_2C_5Br_4$) have been prepared by the low-temperature reaction of Pt(C_2H_4)(PPh$_3$)$_2$ and the given diazo molecule. Like the nickel analogues these platinum complexes are unstable in solution above −50 °C and slowly decompose in the solid state. The $N_2C_5Cl_4$ complex exhibits a medium intensity infrared band at 1496 cm^{-1} which we assign to ν(NN). The $N_2C_5Br_4$ complex exhibits a broad shoulder in this region (1490 cm^{-1}); this NN stretching frequency is partially obscured by triphenylphosphine bands at ca. 1480 cm^{-1} and thus cannot be assigned with certainty. Once again on the basis of infrared spectral evidence, the diazo molecules in these platinum complexes are coordinated in the η^2 manner. These systems are stereochemically rigid, as low-temperature ^{31}P NMR spectra consist of a doublet of doublets pattern of an AB system (Table II); the magnitudes of ^2J(PP) for the cis-phosphine ligands are comparable with those in *cis*-PtCl$_2$PP′ systems.[37]

Thermolysis of "Ni($N_2C_5H_4$)(PPh$_3$)$_2$" in the Presence of Diethyl Maleate. Diazomethane and diazofluorene are catalytically decomposed by various nickel(0) or palladium(0) complexes in the presence of an excess of olefin to give cyclopropanation products. These products are derived from the direct reaction of nickel(0)–carbene complexes with the olefin.[16] However, when diazocyclopentadienes ($N_2C_5X_4$) are used as potential carbene precursors with Ni(0), no cyclopropane products are obtained; instead we obtain (triphenylphosphonium)cyclopentadienylidene (4).[19] Diazo molecules, such as diazocyclopentadiene and diphenyldiazomethane, are known[38] to react with triphenylphosphine to form the corresponding "phosphazine" compounds **1** and **2**. When **2** is heated to 185 °C in vacuo, (diphenylmethylene)triphenylphosphorane (**3**) is obtained.[38] All attempts to effect thermal decomposition of **1** to **4** have failed.[38] However, thermal decomposition of "Ni($N_2C_5H_4$)(PPh$_3$)$_2$", generated in situ from Ni(C_2H_4)(PPh$_3$)$_2$ and $N_2C_5H_4$, yields the (tri-



---

(34) Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 50–1.

(35) Dickson, R. S.; Ibers, J. A. *J. Organomet. Chem.* **1972**, *36*, 191–207.

(36) Stalick, J. K.; Ibers, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 5333–8.

(37) Allen, F. H.; Sze, S. N. *J. Chem. Soc. A* **1971**, 2054–6.

(38) Ramirez, F.; Levy, S. *J. Org. Chem.* **1958**, *23*, 2036–7.

phenylphosphonium)cyclopentadienylidene product (**4**). One can envision two means of ylide formation: (a) the diazo ligand may attack the nickel–phosphine complex to form the "phosphazine" (**1**) which decomposes in the presence of the metal to the ylide (**4**) or (b) the nickel–diazo complex decomposes to form a carbene species $(PPh_3)_2Ni{=}C_5H_4$ which preferentially attacks triphenylphosphine rather than diethyl maleate to form **4**.

The reaction chemistry of diazocyclopentadienes coordinated to Ni(0) is thus very different from that observed for diazomethane or diazofluorene Ni systems. Perhaps the ability of the cyclopentadienyl carbene species $:C_5H_4$ to stabilize electron density on the "carbenoid" carbon atom by delocalization into a C_5 aromatic system is one reason for the differing reaction chemistry. Such stabilization would tend to diminish the carbenoid character of the C(1) carbon atom and thus inhibit its reaction as a carbene with olefins to produce cyclopropane products. In fact the stabilization of the carbene by aromatization would tend to make the C(1) carbon atom more positive in character and thus facilitate its reaction with electron-donor species, such as triphenylphosphine, to give ylide products.

Acknowledgments. We are indebted to Johnson Matthey, Inc., for the loan of precious metals used in this study. This work was kindly supported by the National Science Foundation (Grant CHE76-10335).

Registry No. I, 73531-57-4; II, 73531-58-5; III, 73531-59-6; IV, 73531-60-9; V, 73531-62-1; VI, 73531-63-2; VII, 73531-64-3; VIII, 73531-65-4; $Ni(C_2H_4)(PPh_3)_2$, 23777-40-4; $Ni(COD)_2$, 1295-35-8; $Ru(CO)_2(C_2H_4)(PPh_3)_2$, 35795-47-2; $[Ru(CO)_2(N_2Ph)(PPh_3)_2][PF_6]$, 56389-71-0; $RuH_2(CO)_2(PPh_3)_2$, 21029-29-8; $Ru(CO)_2(PPh_3)_3$, 35880-54-7; $Ni(t\text{-}BuNC)_2$, 29564-99-6; $Ni(N_2C_5Cl_4)(PPh_3)_2$, 73531-66-5; $Ni(N_2C_5H_4)(PPh_3)_2$, 73531-67-6; $Ph_3PC_5H_4$, 29473-30-1; $Pt(C_2H_4)(PPh_3)_2$, 12120-15-9; diethyl maleate, 141-05-9.

Supplementary Material Available: Table VI, the idealized positions of the hydrogen atoms, Table VII, the root-mean-square amplitudes of vibration, and the listing of observed and calculated structure amplitudes (22 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratoire de Chimie de Coordination du CNRS associé l'Université Paul Sabatier,
31400 Toulouse, France, and the Department of Chemistry, Northwestern University, Evanston, Illinois 60201

Electrophilic Addition of a Proton to 1,2-Bis(carbomethoxy)acetylene Inserted into the Iron–Iron Bond of $[(\mu\text{-}SCH_3)Fe(CO)(P(CH_3)_3)_2]_2$. X-ray Structure at −162 °C of the Reaction Product, a Chelated 1,2-Bis(carbomethoxy)ethylene Complex, $[((\mu\text{-}SCH_3)Fe(CO)(P(CH_3)_3)_2)_2(CH_3COOCCHCOOCH_3)][B(C_6H_5)_4]$

J. J. BONNET,[1a] R. MATHIEU,*[1a] and JAMES A. IBERS*[1b]

Received December 26, 1979

The synthesis and structure from IR and NMR data of the complex $((\mu\text{-}SCH_3)Fe(CO)(P(CH_3)_3)_2)_2(CH_3COOCCCOOCH_3)$ are described, and its reactivity toward H^+ is studied. Protonation gives a chelated (C,O) 1,2-bis(carbomethoxy)ethylene complex in which the added proton is cis to the carbon-bonded iron atom. The structure of the product has been established by a crystal structure determination of $[((\mu\text{-}SCH_3)Fe(CO)(P(CH_3)_3)_2)_2(CH_3COOCCHCOOCH_3)][B(C_6H_5)_4]$. In this complex each iron atom is octahedrally coordinated to two bridging sulfur atoms of the methylthiolato groups, two phosphine ligands trans to the sulfur atoms, one carbonyl group, and a vinylic carbon atom for one iron atom and an oxygen atom of the α-carbonyl ester group for the other. The compound crystallizes with 4 formula units in the monoclinic space group $C_{2h}^5\text{-}P2_1/c$ in a cell of dimensions $a = 10.716$ (4) Å, $b = 30.227$ (11) Å, $c = 16.346$ (5) Å, and $\beta = 102.75$ (1)°. On the basis of 5856 unique reflections, the structure was refined by full-matrix least-squares techniques to conventional indices (on F) of $R = 0.050$ and $R_w = 0.057$. The Fe–Fe separation of 3.452 (1) Å and the dihedral angle around the sulfur atoms of 157.8° lead to the widest spacing thus far found for this type of dinuclear, sulfur-bridged iron complex.

Introduction

The reaction of alkynes with transition-metal hydrides to give alkene complexes is well-known and has been extensively studied.[2] It has also been found that protonation of mononuclear alkyne complexes of platinum, palladium,[3,4] and osmium[5] gives alkene complexes.

We have shown recently[6] that photochemical activation induces the insertion of an alkyne into the iron–iron bond of $[(\mu\text{-}A)Fe(CO)_3]_2$ complexes ($A = SCH_3, SC_6H_5, P(CH_3)_2$), and it was of interest to determine if the double σ-bonded alkynes in these complexes have the same type of reactivity as do alkynes in mononuclear complexes. If protonation occurs, we expected the product to be a σ–π alkene complex, as has been encountered in the reaction of methyl vinyl sulfide with Fe_3CO_{12}[7] and in the reaction of ethylene with $H_2Os_3CO_{10}$.[8,9] We thus undertook a study of the protonation of $(\mu\text{-}SCH_3)_2Fe_2(CO)_{6-n}(P(CH_3)_3)_n(CH_3COOCCCOOCH_3)$

---

[1] (a) CNRS. (b) Northwestern University.

[2] Muetterties, E. L. "Transition Metal Hydrides"; Marcel Dekker: New York, 1971; pp 256, 306.

[3] Mann, B. E.; Shaw, B. L.; Tucker, N. I. *J. Chem. Soc. A* **1971**, 2667–2673.

[4] Kemmit, R. D. W.; Kimura, B. Y.; Littlecott, G. W. *J. Chem. Soc., Dalton Trans.* **1973**, 636–640.

[5] Cooke, M.; Green, M.; Kuc, T. A. *J. Chem. Soc. A* **1971**, 1200–1203.

[6] Mathieu, R.; Poilblanc, R. *J. Organomet. Chem.* **1977**, *142*, 351–355.

[7] King, R. B.; Treichel, P. M.; Stone, F. G. A. *J. Am. Chem. Soc.* **1961**, *83*, 3600–3604.

[8] Keister, J. B.; Shapley, J. R. *J. Organomet. Chem.* **1975**, *85*, C29–C31.

[9] Deeming, A. J.; Hans, S.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1975**, 1614–1620.

0020-1669/80/1319-2448$01.00/0