Reactions of Gaseous Nitric Oxide with Anionic Ruthenium Carbide Carbonyl Clusters

Teiji Chihara,[†] Koushi Sawamura,[‡] Hidenori Ikezawa,[†] Haruo Ogawa,[‡] and Yasuo Wakatsuki*,[†]

The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-01, Japan, and Department of Chemistry, Tokyo Gakugei University, Koganei, Tokyo 184, Japan

Received July 24, 1995[⊗]

Gaseous nitric oxide reacted with the dianionic hexanuclear ruthenium carbide cluster $[PPN]_2[Ru_6C(CO)_{16}]$ (PPN = $(PPh_3)_2N$) to give the monoanionic nitrosyl complex $[PPN][Ru_6C(CO)_{15}(NO)]$ (**2**) in good yield. On further reaction with gaseous NO, **2** gave a neutral pentanuclear complex with NO and NO_2 ligands, $Ru_5C(CO)_{14}(NO)(NO_2)$, the structure of which was confirmed by X-ray analysis of the phosphine derivative $Ru_5C(CO)_{13}(PPh_3)(NO)(NO_2)$ (**4**). A monoanionic allyl derivative of the hexanuclear ruthenium cluster, $[PPN][Ru_6C(CO)_{15}(C_3H_5)]$, reacted with NO to give neutral hexa- and pentanuclear allyl complexes with NO (and NO_2) ligands, $Ru_6C(CO)_{14}(C_3H_5)(NO)$ (**6**) and $Ru_5C(CO)_{11}(C_3H_5)(NO)_2(NO_2)$ (**7**). Addition of gaseous NO to **6** gave rise to another pentanuclear complex $Ru_5C(CO)_{13}(C_3H_5)(NO_2)$ (**8**) which did not react further with NO. The solid state structures of the new NO and NO_2 complexes **4** and **6**−**8** are reported.

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on January 9, 1996 on http://pubs.acs.org | doi: 10.1021/om950570l

Introduction

Reduction of NO in the exhaust gases of combustion engines by heterogeneous catalysts has been investigated using ammonia,[1] hydrogen,[2] carbon monoxide,[3] and/or hydrocarbons[4] as reducing agents. The first stage of such processes has been supposed to by adsorption of the gaseous reductant and NO on the metal surfaces. Fixation of gaseous NO on a metal carbonyl cluster is of importance as a model for the initial step in CO-promoted NO reduction which occurs on the surface of heterogeneous metal catalysts.[5] If a hydrocarbon ligand is present, the relative orientation of NO, CO, and the hydrocarbon ligand in a cluster complex, as well as their successive reaction, are also interesting as a model. One of the most promising processes for the NO reduction in diesel engine exhaust is reduction by hydrocarbons on a supported metal surface.[6]

The coordination of gaseous (and neutral) NO molecules to metal carbonyl clusters has only few precedents. In 1972 Collman and co-workers reported the reaction of $M_3(CO)_9$ (M = Ru, Os) with gaseous NO in boiling benzene to give $M_3(CO)_{10}(NO)_2$ which was isolated in 29% (Ru) and 13% (Os) yields and was analyzed to consist of two bridging nitrosyl ligands on the same edge of the metal triangle.[7] Since $M_3(CO)_{10}(NO)_2$ is unstable under the reaction conditions giving insoluble and uncharacterizable polymeric material, reproduction of this reaction is rather difficult and yields are much lower by our hands. Very recently, $[Ir_6(CO)_{14}(NO)]^-$ was prepared via one-electron oxidation of $[Ir_6(CO)_{15}]^{2-}$ followed by addition of NO.[8]

The vast majority of nitrosyl carbonyl clusters have been prepared using nitrosonium cations or nitrite anions as source of the NO ligand because direct reaction of NO gas usually leads to decomposition of the carbonyl cluster frameworks.[5] One problem in using gaseous NO is that it donates three electrons to metal frames and the third electron has been believed to be responsible for metal−metal bond cleavage. Our general strategy for direct fixation of gaseous NO on metal carbonyl clusters has been (1) to use cluster complexes with strong metal−metal frameworks and (2) to employ anionic clusters which are expected to be more susceptible to redox reactions than their neutral analogs. In this paper we report on reactions of anionic hexanuclear ruthenium carbide complexes which meet these conditions with NO. Further reactions of the resulting neutral nitrosyl complexes with NO, which lead to a release of the excess electron accumulated on the cluster by nuclearity reduction, are also described. Parts of these result have been communicated before.[9]

Results and Discussion

1. Reaction of $[PPN]_2[Ru_6C(CO)_{16}]$. On bubbling of NO gas slowly through an orange-red CH_2Cl_2 solution of $[PPN]_2[Ru_6C(CO)_{16}]$ (**1**) (PPN = $(PPh_3)_2N$) at room temperature, the color gradually turned to red-brown. The reaction was continued until the strong ν(CO) band of **1** at 1977 cm^{-1} disappeared, while a new band at 2022 cm^{-1} increased. Workup of the mixture by column

---

* Author to whom correspondence should be addressed.
[†] The Institute of Physical and Chemical Research.
[‡] Tokyo Gakugei University.
[⊗] Abstract published in *Advance ACS Abstracts*, December 1, 1995.

(1) Bsch, H. *Catal. Today* **1987**, 1.

(2) Shelef, M. *Catal. Rev.—Sci. Eng.* **1975**, *11*, 1.

(3) Eisenberg, R.; Hendricksen, D. E. *Adv. Catal.* **1979**, *28*, 79 and references therein.

(4) (a) Sato, S.; Yu-u, Y.; Yashiro, H.; Mizuno, N.; Iwamoto, M. *Appl. Catal.* **1991**, *70*, L1. (b) Shelef, M. *Chem Rev.* **1995**, *95*, 209 and references therein.

(5) Gladfelter, W. L. *Adv. Organomet. Chem.* **1985**, *24*, 41 and references therein.

(6) Inui, T.; Iwamoto, S.; Shimizu, S. *Proc. 9th Inter. Zeolite Confer.* **1992**, *II*, 405.

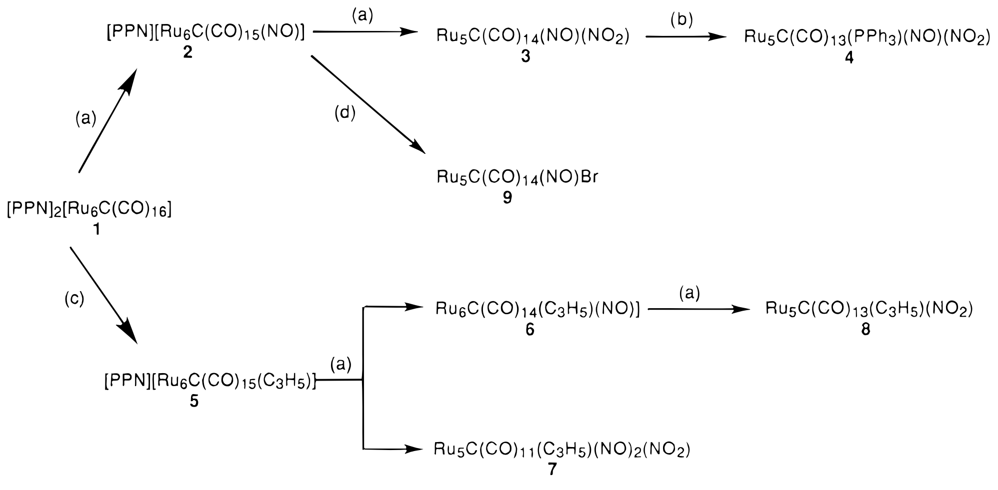
(7) (a) Norton, J. R.; Collman, J. P.; Dolcetti, G.; Robinson, W. T. *Inorg. Chem.* **1972**, *11*, 382. (b) Norton, J. R.; Dolcetti, G. *Inorg. Syn.* **1976**, *16*, 39.

(8) Pergola, R. D.; Garlaschelli, L.; Manassero, M.; Masciocchi, N. *J. Organomet. Chem.* **1995**, *488*, 199.

(9) Chihara, T.; Sawamura, K.; Ogawa, H.; Wakatsuki, Y. *J. Chem. Soc., Chem. Commun.* **1994**, 1179.

0276-7333/96/2315-0415$12.00/0 © 1996 American Chemical Society

Scheme 1



(a) NO gas, r.t; (b) PPh_3, r.t.; (c) C_3H_5Br, 115 °C; (d) Br_2, r.t.

chromatography gave red crystals of $[PPN][Ru_6C(CO)_{15}(NO)]$ (**2**) in 85% yield (eq 1). This complex has been

$$\underset{\textbf{1}\ \ 86e}{[Ru_6C(CO)_{16}]^{2-}} \xrightarrow{NO} \underset{\textbf{2}\ \ 86e}{[Ru_6C(CO)_{15}(NO)]^-} \qquad (1)$$

prepared previously by the reaction of neutral $Ru_6C(CO)_{17}$ with $[PPN][NO_2]$ as reported by Gladfelter[10] and Johnson[11] and has been proved to have a terminal NO ligand. In our reaction, it is noteworthy that the neutral NO, which is a three electron donor, has replaced one carbonyl ligand and one negative charge,[12] formally "a carbonyl anion", the electron count of both **1** and **2** being 86. An important factor for this smooth reaction appears to be the presence of the anionic charge on the starting complex **1**, which probably promotes the facile redox reaction 1. We have previously observed a similar smooth redox reaction of a monoanionic trinuclear Ru cluster with gaseous NO, which gave a neutral Ru_3–NO complex.[9]

Since in complex **2** one negative charge is left, further reaction with gaseous NO was expected to replace "CO^-" again and give a neutral bis(nitrosyl) complex. The reaction of **2** with NO gas took place easily; the NO gas was bubbled slowly through a CH_2Cl_2 solution of **2** until the IR absorption band at 2022 cm^{-1} disappeared. The intensity of new peaks at 2087 and 2067 cm^{-1} was increasing, and the color of the reaction mixture changed from red-brown to yellow-brown. However, the green complex isolated from the reaction mixture in 23% yield was not the expected bis(nitrosyl) cluster but had a different nuclearity; i.e., the composition was $Ru_5C(CO)_{14}(NO)(NO_2)$ (**3**) as suggested by FAB-mass spectroscopy and elemental analysis.[13] Since single crystals of this complex could not be obtained, **3** was further reacted with PPh_3 (Scheme 1). A yellow-green single crystal of the phosphine derivative $Ru_5C(CO)_{13}(PPh_3)(NO)(NO_2)$ (**4**) was structurally characterized to display a molecular geometry as shown in Figure 1. Selected interatomic distances and bond angles are listed in Table 1.

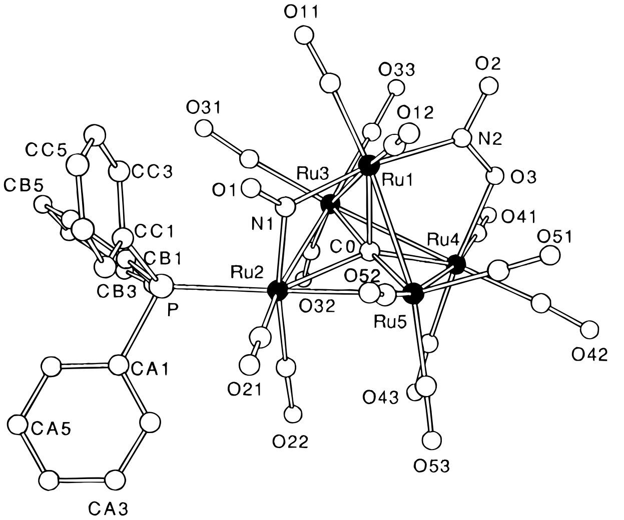


Figure 1. Molecular structure of $Ru_5C(CO)_{13}(NO)(NO_2)PPh_3$ (**4**). Carbonyl carbons have the same numbering as their oxygen counterparts but are omitted for clarity. The first digit of each oxygen number is the number of the ruthenium atom to which the carbonyl is attached.

The five nuclear metal framework has a distorted square-based pyramidal structure with an interstitial carbide atom. The metal–metal-bonding distances of 2.840(1)–2.958(1) Å are within the expected range.[14] Two of the edges of the metal frame are bridged by NO and NO_2 units, where a direct metal–metal bond does not exist, the distances Ru1–Ru2 being 3.2407(5) Å and Ru1–Ru4 being 3.5615(4) Å. The electron count of 78 for **3** and **4** (counting NO and NO_2 as three electron donors) is four electrons more than expected for regular

---

[10] Stevens, R. E.; Gladfelter, W. L. *Inorg. Chem.* **1983**, *22*, 2034.

[11] Johnson, B. F. G.; Lewis, J.; Nelson, W. J. H.; Puga, J.; Raithby, P. R.; Braga, D.; McPartlin, M.; Clegg, W. *J. Organomet. Chem.* **1983**, *243*, C13.

[12] If the electron released from the starting complex in reactions **1** → **2** and **5** → **6** ultimately reacts with the solvent is not quite clear yet: we carried out the reaction of **5** with NO in different solvents (CH_2Cl32, THF, acetone, benzene) and observed that the reaction in CH_2Cl_2 was the smoothest and cleanest one.

[13] The reaction of **2** in a closed system with an equimolar amount of NO at room temperature overnight resulted in the formation of **3** in a few percent conversion while a large amount of **2** remained unreacted as monitored by IR spectroscopy. Since no appreciable new peak was observed in the IR ν(CO) region under these conditions, the reaction of the assumed neutral hexanuclear bis(nitrosyl) complex with gaseous NO appears to be faster than its formation from **2** and NO.

[14] Chihara, T.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1995**, 1369.

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on January 9, 1996 on http://pubs.acs.org | doi: 10.1021/om9505701

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $Ru_5C(CO)_{13}(PPh_3)(NO)(NO_2)$ (4)

Ru1···Ru2	3.2407(5)	Ru5−C0	1.960(3)
Ru1−Ru3	2.8412(5)	Ru1−N1	1.995(3)
Ru1···Ru4	3.5615(4)	Ru1−N2	2.135(3)
Ru1−Ru5	2.8398(5)	Ru2−P	2.401(1)
Ru2−Ru3	2.9577(4)	Ru2−N1	2.070(3)
Ru2−Ru5	2.9000(6)	Ru4−O3	2.126(3)
Ru3−Ru4	2.8712(5)	P−CA1	1.848(3)
Ru4−Ru5	2.8715(5)	P−CB1	1.830(4)
Ru1−C0	2.119(3)	P−CC1	1.827(3)
Ru2−C0	2.141(3)	O1−N1	1.204(3)
Ru3−C0	1.941(3)	O2−N2	1.221(4)
Ru4−C0	2.120(3)	O3−N2	1.307(4)
Ru2−Ru1−N1	37.93(8)	O2−N2−O3	114.7(3)
Ru4−Ru1−N2	58.11(8)	Ru1−C0−Ru2	99.1(1)
N1−Ru1−N2	169.4(1)	Ru1−C0−Ru3	88.7(1)
Ru1−Ru2−N1	36.34(7)	Ru1−C0−Ru4	114.3(2)
Ru1−Ru4−O3	57.97(6)	Ru1−C0−Ru5	88.2(1)
Ru4−O3−N2	122.4(2)	Ru2−C0−Ru3	92.7(2)
Ru1−N1−Ru2	105.7(1)	Ru2−C0−Ru4	146.6(2)
Ru−N1−O1	125.2(3)	Ru2−C0−Ru5	89.9(1)
Ru2−N1−O1	128.7(2)	Ru3−C0−Ru4	89.9(1)
Ru1−N2−O2	123.9(2)	Ru3−C0−Ru5	176.2(2)
Ru1−N2−O3	121.4(2)	Ru4−C0−Ru5	89.4(1)

square pyramidal metal frames and in accord with the breakage of the two metal−metal bonds. Since the Ru1−Ru4 bond is bridged by the two atoms (N2−O3) of the NO_2 unit, the metal−metal distance is particularly long and the basal plane of the square pyramid is forced to bend by 36.35(1)°. The interstitial carbon atom is bonded to all the five metal atoms, suggesting its important role of keeping the metal skeleton stable despite its highly distorted structure.

Another example for reduction of cluster nuclearity was found in the reaction of **2** with bromine. The reaction took place instantaneously at room temperature in a CH_2Cl_2 solution to give a neutral product isolated as green crystals. The composition of $Ru_5C(CO)_{14}(NO)Br$ (**9**) was determined by elemental analysis and confirmed unequivocally by a FAB-mass spectrum. The IR absorption of **9** in the ν(CO) region is quite similar to that of **3** and $Ru_5C(CO)_{14}Br_2$.[14] The metal framework of the latter complex has been reported previously to be similar to that of **3**; i.e. the two Br ligands function as three electron donors and occupy the same positions as the NO and NO_2 ligands in **3**. The structure of **9**, therefore, should be similar to that of **3** with the Br lgiand playing the role of NO_2 bridging two nonbonded metal atoms.

2. Reaction of [PPN][$Ru_6C(CO)_{15}(C_3H_5)$]. The μ,η^3-allyl complex [PPN][$Ru_6C(CO)_{15}(C_3H_5)$] (**5**), which has been prepared previously in this laboratory,[15] was treated with gaseous NO. A red CH_2Cl_2 solution of **5** turned red-brown on bubbling NO gas through it. The reaction was conveniently monitored by the gradual disappearance of the IR ν(CO) bands of **5** at 2000 and 2012 cm^{-1} while new peaks at 2046 and 2054 cm^{-1} increased as the reaction proceeded. Two neutral complexes were isolated from the reaction mixture, a red hexanuclear complex $Ru_6C(CO)_{14}(C_3H_5)(NO)$ (**6**) isolated in 30% yield and an orange colored pentanuclear complex $Ru_5C(CO)_{11}(C_3H_5)(NO)_2(NO_2)$ (**7**) isolated in 11% yield (Scheme 1). Both complexes were characterized by X-ray analysis to have the structures shown in Figures 2 and 3. Selected interatomic distances and bond angles are listed in the Tables 2 and 3, respectively. The reaction could also be carried out in a closed system: addition of 7 equiv NO by a syringe to a CH_2Cl_2 solution of **5** gave after 1 day stirring at room temperature complex **6** in 37% yield.[16] In the presence of an equimolar amount of $(NH_4)_2Ce(NO_3)_6$ the reaction proceeded much faster, several hours at 0 °C to completion, but the yield of **6** was not improved. The formation of **7** was not observed under these conditions; instead a green colored uncharacterizable powder was obtained.

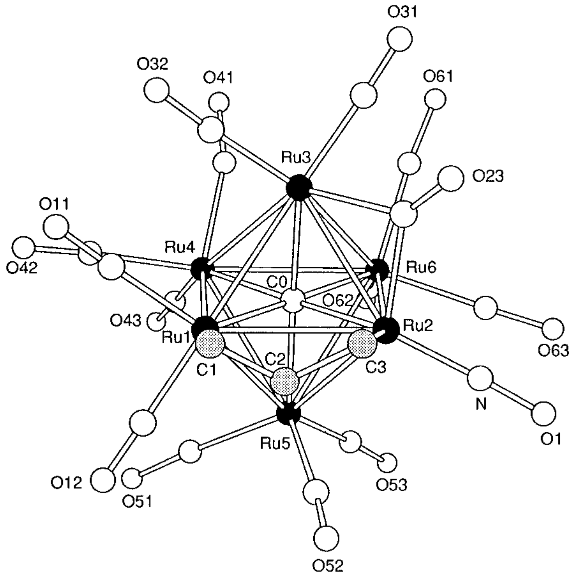


Figure 2. Molecular structure of $Ru_6C(CO)_{14}(C_3H_5)(NO)$ (**6**) showing the atom-numbering scheme.

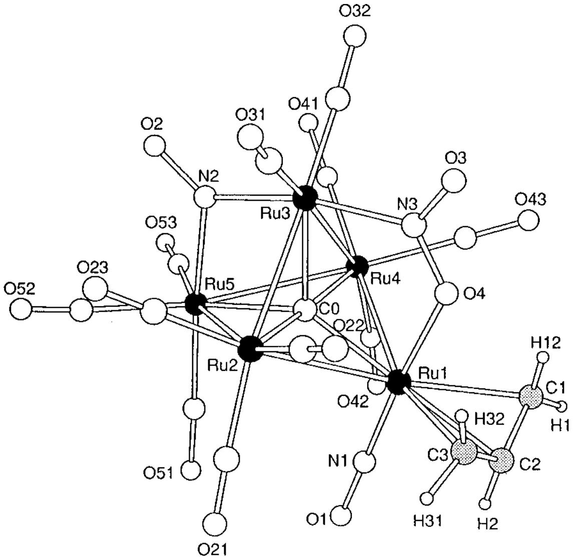


Figure 3. Molecular structure of $Ru_5C(CO)_{11}(C_3H_5)(NO)_2(NO_2)$ (**7**) showing the atom-numbering scheme.

The solid state structure of complex **6** (Figure 2) has a metal−allyl framework similar to that of the parent complex [$Ru_6C(CO)_{15}(C_3H_5)$]$^-$. Interestingly, a terminal NO is bonded to the same metal atom to which one of the allyl terminal carbons is also coordinated. A 400

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on January 9, 1996 on http://pubs.acs.org | doi: 10.1021/om9505701

---

(15) Chihara, T.; Aoki, K.; Yamazaki, H. *J. Organomet. Chem.* **1990**, *383*, 367.

(16) With an equimolar amount of NO the reaction was too slow, and thus a large amount of unreacted material was recovered after 24 h.

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on January 9, 1996 on http://pubs.acs.org | doi: 10.1021/om950570l

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $Ru_6C(CO)_{14}(C_3H_5)(NO)$ (6)

Ru1–Ru2	2.9814(10)	Ru5–C0	2.053(6)
Ru1–Ru3	2.9264(8)	Ru6–C0	2.060(9)
Ru1–Ru4	2.8415(9)	Ru1–C1	2.213(10)
Ru1–Ru5	2.8902(9)	Ru1–C2	2.460(10)
Ru2–Ru3	2.8110(10)	Ru2–N	1.759(8)
Ru2–Ru5	2.9574(10)	Ru2–C2	2.721(9)
Ru2–Ru6	2.8925(10)	Ru2–C3	2.191(10)
Ru3–Ru4	2.9273(10)	Ru2–C23	2.057(8)
Ru3–Ru6	2.9111(9)	Ru3–C23	2.088(10)
Ru4–Ru5	2.9122(10)	Ru3–C41	2.639(10)
Ru4–Ru6	2.8811(10)	Ru4–C41	1.944(9)
Ru5–Ru6	2.8591(9)	O1–N	1.17(1)
Ru1–C0	2.0312(9)	O23–C23	1.16(1)
Ru2–C0	2.052(11)	O41–C41	1.13(1)
Ru3–C0	2.049(6)	C1–C2	1.40(1)
Ru4–C0	2.057(11)	C2–C3	1.44(1)
Ru2–Ru1–C1	89.0(3)	Ru1–C1–C2	82.5(6)
Ru2–Ru1–C2	59.1(2)	Ru1–C2–Ru2	70.1(2)
C1–Ru1–C2	34.4(3)	Ru1–C2–C1	63.1(5)
Ru1–Ru2–C2	50.9(2)	Ru1–C2–C3	114.7(6)
Ru1–Ru2–C3	78.5(3)	Ru2–C2–C1	123.3(7)
Ru3–Ru2–C23	47.8(3)	Ru2–C2–C3	53.4(5)
C2–Ru2–C3	31.8(3)	C1–C2–C3	123.8(9)
N–Ru2–C2	109.3(4)	Ru2–C3–C2	94.8(6)
N–Ru2–C3	91.5(4)	Ru1–C23–Ru3	85.4(3)
N–Ru2–C23	106.5(4)	Ru2–C23–O23	136.8(7)
C2–Ru2–C23	101.5(3)	Ru3–C23–O23	137.7(7)
C3–Ru2–C23	82.0(4)	Ru3–C41–Ru4	77.8(3)
Ru2–Ru3–C23	46.8(2)	Ru3–C41–O41	121.3(7)
Ru2–N–O1	170.6(8)	Ru4–C41–O41	160.9(9)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $Ru_5C(CO)_{11}(C_3H_5)(NO)_2(NO_2)$ (7)

Ru1–Ru2	2.8702(11)	Ru1–C2	2.221(10)
Ru1···Ru3	3.5807(10)	Ru1–C3	2.265(9)
Ru1–Ru4	2.8717(10)	Ru3–N2	1.979(7)
Ru2–Ru3	2.8555(11)	Ru3–N3	2.113(7)
Ru2–Ru5	2.8916(10)	Ru5–N2	2.063(7)
Ru3–Ru4	2.8472(10)	O1–N1	1.164(10)
Ru3···Ru5	3.2223(10)	O2–N2	1.225(10)
Ru4–Ru5	2.8844(11)	O3–N3	1.220(9)
Ru1–C0	2.059(8)	O4–N3	1.305(9)
Ru2–C0	1.949(8)	C1–C2	1.42(1)
Ru3–C0	2.098(8)	C1–H11	1.00(7)
Ru4–C0	1.973(8)	C1–H12	0.92(9)
Ru5–C0	2.144(8)	C2–C3	1.36(1)
Ru1–O4	2.111(6)	C2–H2	0.89(8)
Ru1–N1	1.722(8)	C3–H31	1.14(8)
Ru1–C1	2.301(8)	C3–H32	0.86(8)
Ru3–Ru1–O4	56.6(2)	Ru1–C0–Ru2	91.4(3)
C1–Ru1–C2	36.6(4)	Ru1–C0–Ru3	118.9(4)
C1–Ru1–C3	65.5(4)	Ru1–C0–Ru4	90.8(3)
C2–Ru1–C3	35.3(4)	Ru1–C0–Ru5	142.2(4)
Ru1–Ru3–N3	58.1(2)	Ru2–C0–Ru3	89.7(4)
Ru5–Ru3–N2	38.1(2)	Ru2–C0–Ru4	177.7(5)
N2–Ru3–N3	167.5(3)	Ru2–C0–Ru5	89.8(3)
Ru3–Ru5–N2	36.3(2)	Ru3–C0–Ru4	88.7(3)
Ru1–O4–N3	124.8(5)	Ru3–C0–Ru5	98.9(3)
Ru1–N1–O1	177.6(7)	Ru4–C0–Ru5	88.9(3)
Ru3–N2–Ru5	105.7(3)	Ru1–C1–C2	68.6(5)
Ru3–N2–O2	129.2(6)	Ru1–C2–C1	74.8(5)
Ru5–N2–O2	125.1(6)	Ru1–C2–C3	74.1(6)
Ru3–N3–O3	125.4(5)	Ru1–C3–C2	70.6(6)
Ru3–N3–O4	120.5(5)	C1–C2–C3	125.1(9)
O3–N3–O4	114.1(7)		

MHz ^1H NMR spectrum measured at room temperature showed a broad singlet of syn-protons at 3.73, a multiplet of the central proton centered at 1.25, and a doublet of a doublet due to anti-protons at 0.37 ppm (J = 12.5, 2.5 Hz). At −70 °C, the two syn-protons (4.10, 3.02 ppm) and the two anti-protons (0.34, −0.11 ppm) are not equivalent in accordance with the solid state structure. Thus, **6** in solution exhibits fluxional behavior which will be discussed in detail elsewhere.[17]

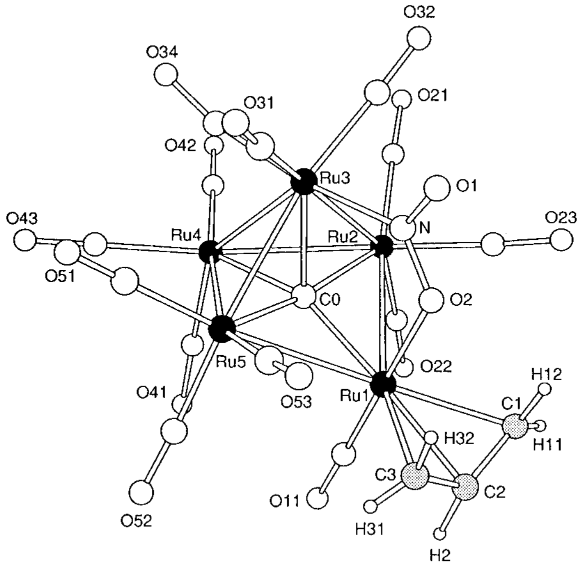


Figure 4. Molecular structure of $Ru_5C(CO)_{13}(C_3H_5)(NO_2)$ (**8**) showing the atom-numbering scheme.

The metal framework of **7** (Figure 3) is essentially the same as **4**, *i.e.* a distorted square pyramid where two of the metal–metal bonds are not directly connected but bridged through NO and NO_2 units. In addition, a terminal NO group is bonded to Ru1 to which the η^3-allyl group is also coordinated. The molecule has a pseudo-mirror plane through the NO and NO_2 units as well as Ru1, Ru3, Ru5, and the interstitial carbide atom. Therefore, the two terminal carbons of the allyl group are equivalent: the ^1H NMR spectrum shows the resonances of the two syn-protons at δ 5.05 (dd, J = 8.2, 1.3 Hz), of the two anti-protons at 2.78 (d, J = 14.2 Hz), and the central protons at 3.92 (tt, J = 14.2, 8.2 Hz) ppm.

Since complex **7** appeared to be formed *via* the initially produced **6**, the reaction of NO gas with **6** was examined. On addition of 3 equiv of gaseous NO to a CH_2Cl_2 solution of **6** at room temperature, smooth reaction took place. After chromatography on silica gel, the product isolated was found to be a five nuclear cluster with a molecular composition $Ru_5C(CO)_{13}(C_3H_5)(NO_2)$ (**8**) containing less NO-derived units than **7**. The solid state structure of **8** (Figure 4) shows that this metal skeleton consists also of a distorted square pyramid only slightly different from **7**. Selected interatomic distances and bond angles are listed in Table 4. In accordance with its electron count of 76, compared to 78 in **7**, one metal–metal bond is absent in **8** and bridged by the NO_2 unit. The position of the η^3-allyl moiety is the same as in **7**, and the molecule has also a pseudo-mirror plane which bisects the allyl group. Contrary to our expectation, **8** was found to be quite stable and did not react further with gaseous NO. At present the route to **7** remains unclear; there should be a direct pathway from **5** by reaction with a large excess NO.

The presence of NO_2 units in the complexes **3**, **7**, and **8** has not been expected from the beginning. Since the generation of **8** from **6** is particularly facile, we examined the reaction in detail aiming at the elucidation of the source of the NO_2 ligand. First, it could be con-

---

[17] Chihara, T.; Ikezawa, H.; Jesorka, A.; Wakatsuki, Y. To be submitted for publication.

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on January 9, 1996 on http://pubs.acs.org | doi: 10.1021/om950570l

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $Ru_5C(CO)_{13}(C_3H_5)(NO_2)$ (8)

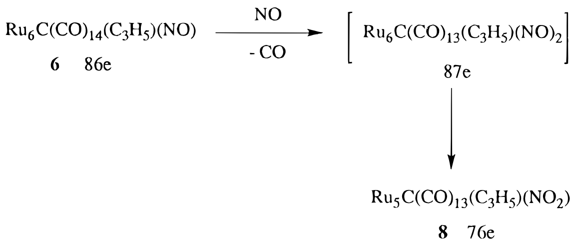
Ru1−Ru2	2.915(2)	Ru1−C2	2.220(11)
Ru1···Ru3	3.608(3)	Ru1−C3	2.224(10)
Ru1−Ru5	2.913(2)	Ru3−N	2.103(8)
Ru2−Ru3	2.836(2)	Ru3−C34	1.904(10)
Ru2−Ru4	2.805(2)	Ru4−C34	2.535(8)
Ru3−Ru4	2.857(2)	O34−C34	1.152(12)
Ru3−Ru5	2.823(2)	O1−N	1.231(11)
Ru4−Ru5	2.820(2)	O2−N	1.281(9)
Ru1−C0	1.996(8)	C1−C2	1.38(1)
Ru2−C0	2.017(7)	C1−H11	1.02(7)
Ru3−C0	2.144(7)	C1−H12	0.76(8)
Ru4−C0	2.030(9)	C2−C3	1.37(1)
Ru5−C0	1.999(7)	C2−H2	0.96(8)
Ru1−O2	2.125(6)	C3−H31	1.08(8)
Ru1−C1	2.226(11)	C3−H32	0.84(8)

Ru3−Ru1−O2	56.5(2)	Ru1−C0−Ru5	93.6(3)
C1−Ru1−C2	36.3(4)	Ru2−C0−Ru3	85.9(3)
C1−Ru1−C3	64.7(4)	Ru2−C0−Ru4	87.7(3)
C2−Ru1−C3	35.8(4)	Ru2−C0−Ru5	171.2(4)
Ru1−Ru3−N	56.7(2)	Ru3−C0−Ru4	86.3(3)
Ru4−Ru3−C34	60.5(3)	Ru3−C0−Ru5	85.8(3)
N−Ru3−C34	169.1(3)	Ru4−C0−Ru5	88.8(4)
Ru3−Ru4−C34	40.8(2)	Ru1−C1−C2	71.6(7)
Ru1−O2−N	122.8(6)	Ru1−C2−C1	72.1(6)
Ru3−N−O1	120.4(6)	Ru1−C2−C3	72.3(6)
Ru3−N−O2	123.9(6)	C1−C2−C3	120.1(8)
O1−N−O2	115.6(8)	Ru1−C3−C2	71.9(6)
Ru1−C0−Ru2	93.2(4)	Ru3−C34−O34	162.7(8)
Ru1−C0−Ru3	121.2(4)	Ru4−C34−O34	118.5(7)
Ru1−C0−Ru4	152.4(4)	Ru3−C34−Ru4	78.7(3)

firmed that complex **6** does not react with free NO_2, indicating that its presence in **8** was not arising by NO ligand replacement by trace amounts of free NO_2 which might be present as an impurity in the NO gas used in the reaction. Addition of an excess amount of O_2 gas to a solution of **6** did not cause appreciable reaction: on standing of the reaction mixture for several hours (long enough time compared to the time scale of reaction **6** → **8**), the starting complex decomposed gradually without any indication of forming meaningful products as monitored by IR spectra. Thus the NO_2 ligand in **8** is apparently not the result of direct oxygenation of NO ligand in complex **6**, a process well-know for mononuclear nitrosyl complexes.[18] Another possible route to NO_2 ligand is via disproportionation reaction of the type: $2NO(g) + ([Ru]{-}NO) \rightarrow N_2O(g) + ([Ru]{-}NO_2)$ where ([Ru]−NO) represents a NO ligand coordinated to a cluster. This reaction type has many precedents in the chemistry of mononuclear nitrosyl complexes, and in most cases the evolved N_2O could be detected in the expected amount.[19] In the case of reaction **6** → **8**, however, we were unable to detect free N_2O by GLC in spite of repeated careful runs.

Until now, we have no positive proof to help elucidate the mechanism of reaction **6** → **8**. Considering that the reduction of the cluster nuclearity, from hexanuclear to pentanuclear, always accompanies the formation of the NO_2 ligand (**2** → **3**, **5** → **7**, **6** → **8**), we tentatively propse a reaction scheme with disproportionation between two coordinated NO units on the cluster which is promoted by splitting-off of one metal unit, the driving force being excess electrons accumulated on the hexanuclear cluster (Scheme 2). Since the number of valence electrons required to form a stable octahedral metal core is 86, the 87 electron bis(nitrosyl) species formed by replacement of one CO group in **6** by NO should be fairly unstable. Formally, removal of one Ru and one N unit, or a “Ru−N” species, would give the observed complex **8** having 76 valence electrons. Loss of a Ru atom reduces 8 electrons and loss of a N atom removes 3 electrons from the cluster, the latter process being the result of $[Ru]{-}(NO)_2 \rightarrow [Ru]{-}NO_2 + N$, and both NO and NO_2 are 3-electron donors. Thus, loss of a “Ru−N” unit will formally correspond to removal of 11 valence electrons. A similar reaction scheme and explanation on the basis of electron count can be applied to the reactions **2** → **3** and **5** → **7**.

Scheme 2



Reaction **2** → **9** (Scheme 1) provides further evidence for our hypothesis that one of the oxygen atoms in the NO_2 ligand originates from another NO unit. The NO ligand in the cluster remains indeed intact in the nuclearity reducing reaction **2** → **9** where a reagent (Br_2) differnt than gaseous NO has been used.

Conclusion

Gaseous NO can readily replace a carbonyl igand and one negative charge (or formally a carbonyl anion) in hexanuclear anionic ruthenium carbonyl clusters to give stable nitrosyl clusters. The octahedral metal framework is retained with the presence of interstitial carbide atom appearing to play an important role: the reaction of the octahedral anionic cluster having no carbide atom, $[PPN]_2[Ru_6(CO)_{18}]$, with NO gas resulted in mere decomposition. The reaction of gaseous NO with neutral hexanuclear carbonyl clusters bearing NO ligands leads to the formation of NO_2 ligands. The NO_2 ligand is probably formed by disproportionation of two NO ligands coordinating to an unstable intermediate with an excess electron, and this process is accompanied by concomitant reduction of the cluster nuclearity. Recent reports on facile metal−metal bond cleavage and reorganization of the metal atom array on solid metal surfaces by adsorption of small molecules are noteworthy.[20]

Experimental Section

The complexes $[PPN]_2[Ru_6C(CO)_{16}]$ (**1**)[21] and $[PPN][Ru_6C(CO)_{15}(C_3H_5)]$ (**5**)[15] were prepared according to the literature methods. NO gas (Sumitomo Seika Chemicals Co., Ltd, “electronic grade”, purity >99.7%) and other reagents were

---

(18) (a) Tamaki, M.; Masuda, I.; Shinra, K. *Bull Chem Soc. Jpn.* **1972**, *45*, 171. (b) Clarkson, S. G.; Basolo, F. *Inorg. Chem.* **1973**, *12*, 1528. (c) Trogler, W. C.; Marzilli, L. G. *Inorg. Chem.* **1974**, *13*, 1008. (d) Ugo, R.; Bhaduri, S.; Johnson, B. F. G.; Khair, A.; Pickard, A.; Benn-Taarit, Y. *J. Chem. Soc., Chem. Commun.* **1976**, 694. (e) Kubota, M.; Phillips, D. A. *J. Am. Chem. Soc.* **1975**, *97*, 5637.

(19) (a) Kiji, S.; Yoshikawa, S.; Furukawa, J. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3614. (b) Rossi, M.; Sacco, A. *Chem. Commun.* **1971**, 694. (c) Gwost, D.; Caulton, K. G. *Inorg. Chem.* **1974**, *13*, 414. (d) Richter-Addo, B.; Legzdins, P. *Metal Nitrosyls*; Oxford University: New York, 1992.

(20) (a) Gritsch, T.; Coulman, D.; Behm, R. J.; Ertl, G. *Appl. Phys.* **1989**, *A49*, 403. (b) Tanaka, H.; Yoshinobu, J.; Kawai, M. *Surface Sci.* **1995**, *327*, L505.

(21) Hayward, T. C.; Shapley, J. R. *Inorg. Chem.* **1982**, *21*, 3816.

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on January 9, 1996 on http://pubs.acs.org | doi: 10.1021/om950570l

Table 5. Crystallographic Data

compd	4	6	7	8
formula	$C_{32}H_{15}N_2O_{16}PRu_5$	$C_{18}H_5NO_{15}Ru_6$	$C_{15}H_5N_3O_{15}Ru_5$	$C_{17}H_5NO_{15}Ru_5$
fw	1219.80	1081.66	972.57	968.57
cryst system	monoclinic	orthorhombic	orthorhombic	triclinic
space group (No.)	$C2/c$ (15)	$pna2_1$ (33)	$P2_12_12_1$ (19)	$P\bar{1}$ (2)
a/Å	25.420(4)	22.571(3)	10.284(1)	17.112(6)
b/Å	14.864(1)	10.693(1)	23.957(3)	17.219(7)
c/Å	21.867(3)	10.915(2)	10.278(1)	9.223(4)
α/deg	90	90	90	92.59(3)
β/deg	108.479(7)	90	90	104.73(3)
γ/deg	90	90	90	85.10(3)
U/Å^3	7836(2)	2634(6)	2532.3(5)	2618(2)
z	8	4	4	4
D_c/g cm^{-3}	2.07	2.72	2.55	2.46
cryst size/mm	0.32 × 0.32 × 0.10	0.43 × 0.41 × 0.07	0.26 × 0.18 × 0.09	0.60 × 0.17 × 0.11
temp/°C	21	21	21	21
λ(Mo Kα)/Å	0.710 73	0.710 73	0.710 73	0.710 73
F(000)	4672	2016	1824	1816
μ/cm^{-1}	19.59	33.64	29.35	28.37
$2\theta_{max}$/deg	55	60	57	55
no. of data measd	9540	4418	3560	12341
no. of unique data used	7088 ($F \geq 3\sigma$)	3735 ($F \geq 3\sigma$)	3169 ($F \geq 3\sigma$)	9307 ($F \geq 3\sigma$)
no. of params	562	631	364	718
corr made	ψ-scan	ψ-scan	no	ψ-scan
transm coeff	0.7344−0.9997	0.3896−0.9987		0.8007−0.9971
final R	0.0294	0.0291	0.0377	0.0534
final R_w	0.0194 ($w = 1/\sigma^2(F_o)$)	0.0302 ($w = 1$)	0.0267 ($w = 1/\sigma^2(F_o)$)	0.0438 ($w = 1/\sigma(F_o)$)
goodness of fit	1.50	2.17	2.09	3.24
maximum Δ/σ	0.456	0.230	0.209	0.306
$\Delta\rho_{map}$/e Å^{-3}	0.51	0.99	1.04	1.30

Table 6. Atomic Coordinates ($\times 10^4$) and Equivalent Temperature Factors (Å^2) for $Ru_5C(CO)_{13}(NO)(NO_2)PPh_3$ (4)

atom	x	y	z	B_{eq}[a]	atom	x	y	z	B_{eq}[a]
Ru1	1818.4(1)	3946.9(2)	1381.6(1)	3.0	C22	3063(1)	5999(2)	2159(2)	3.3
Ru2	2697.4(1)	5507.9(2)	1343.2(1)	2.5	C31	2544(1)	3770(2)	285(2)	3.2
Ru3	1940.9(1)	4577.7(2)	207.7(1)	2.5	C32	2016(2)	5296(2)	−499(2)	3.6
Ru4	1046.1(1)	5657.5(2)	338.4(1)	3.0	C33	1413(2)	3733(2)	−316(2)	3.7
Ru5	1691.8(1)	5778.6(2)	1676.7(1)	3.0	C41	658(2)	5393(2)	−557(2)	3.9
P	3601.1(4)	5219.4(6)	1258.7(5)	2.8	C42	456(2)	6347(3)	504(2)	4.4
O1	2950(1)	3899(2)	2196(1)	5.2	C43	1319(2)	6729(2)	106(2)	3.6
O2	676(1)	3160(2)	937(1)	5.8	C51	1018(2)	5601(3)	1861(2)	4.9
O3	664(1)	4473(2)	544(1)	4.0	C52	2096(2)	5608(3)	2569(2)	4.3
O11	2099(2)	2051(2)	1068(2)	7.4	C53	1709(2)	7082(3)	1669(2)	4.3
O12	1719(2)	3391(2)	2680(1)	7.4	CA1	4078(1)	6192(2)	1441(2)	2.8
O21	2604(1)	7334(2)	682(1)	5.3	CA2	3939(1)	7017(2)	1627(2)	3.4
O22	3280(1)	6282(2)	2660(1)	5.4	CA3	4314(2)	7735(3)	1737(2)	4.2
O31	2873(1)	3250(2)	327(1)	4.8	CA4	4819(2)	7619(3)	1651(2)	4.4
O32	2027(1)	5731(2)	−919(1)	5.9	CA5	4959(2)	6804(3)	1466(2)	5.4
O33	1105(1)	3225(2)	−608(2)	6.1	CA6	4597(2)	6090(3)	1367(2)	4.8
O41	442(1)	5239(2)	−1083(1)	5.6	CB1	3694(2)	4881(2)	495(2)	3.4
O42	128(1)	6787(2)	600(2)	7.0	CB2	3405(2)	5368(3)	−51(2)	4.0
O43	1458(1)	7389(2)	−50(1)	5.6	CB3	3497(2)	5206(3)	−638(2)	5.6
O51	620(1)	5477(3)	1984(2)	8.4	CB4	3874(2)	4559(3)	−667(2)	7.0
O52	2322(1)	5471(2)	3103(1)	7.1	CB5	4156(2)	4045(3)	−149(2)	6.2
O53	1724(2)	7839(2)	1625(2)	7.1	CB6	4071(2)	4227(3)	440(2)	4.9
N1	2614(1)	4293(2)	1766(1)	3.4	CC1	3962(1)	4383(2)	1857(2)	3.2
N2	948(1)	3825(2)	904(1)	3.9	CC2	3885(2)	3467(3)	1735(2)	4.4
C0	1833(1)	5208(2)	936(2)	2.5	CC3	4123(2)	2850(3)	2210(2)	5.5
C11	1978(2)	2754(3)	1170(2)	4.3	CC4	4421(2)	3131(3)	2816(2)	5.7
C12	1751(2)	3597(3)	2196(2)	4.6	CC5	4487(2)	4020(3)	2947(2)	5.1
C21	2643(1)	6646(2)	909(2)	3.2	CC6	4264(2)	4654(3)	2471(2)	4.0

[a] $B_{eq} = 4/3(\sum_i\sum_j B_{ij}a_ib_j)$.

commercially available and used as received. Solvents were dried and distilled under argon before use. All reactions and successive purifications were carried out under argon. IR and ^{1}H NMR spectra were recorded on a Perkin-Elmer 1600 spectrophotometer and a JEOL RX-270 or a JEOL GX-400 spectrometer. FAB-MS spectra were obtained with a JEOL JMS-HX 110A double-focusing spectrometer using *m*-nitrobenzyl alcohol as a liquid matrix.

Reaction of $[PPN]_2[Ru_6C(CO)_{16}]$ (1) with NO. Through a stirred CH_2Cl_2 solution (80 mL) of **1** (1.0 g, 0.46 mmol) in a 200 mL flask NO gas was bubbled slowly (one bubble/s). During 30 min the color turned from red to red-brown. After 4 h the solution was concentrated under reduced pressure and chromatographed on silica gel. A red band eluted with CH_2Cl_2 was collected and concentrated (5 mL), and to this solution was added methanol (5 mL). Red crystals formed (85% yield) were confirmed to be the known complex $[PPN][Ru_6C(CO)_{15}(NO)]$ (**2**) by elemental analysis and IR spectroscopy.[10,11]

Reaction of $[PPN][Ru_6C(CO)_{15}(NO)]$ (2) with NO. Complex **2** (250 mg, 0.156 mmol) was placed in a 100 mL round bottom flask, CH_2Cl_2 (20 mL) was added, and NO gas was bubbled slowly through the solution (one bubble/s) under stirring. During 30 min the color turned from red to yellow-brown. After 7 h the reaction mixture was concentrated and

Table 7. Atomic Coordinates (×10^4) and Equivalent Temperature Factors (Å^2) for $Ru_6C(CO)_{14}(C_3H_5)(NO)$ (6)

atom	x	y	z	B_{eq}[a]	atom	x	y	z	B_{eq}[a]
Ru1	3891.2(2)	4322.8(6)	4566.3(6)	2.6	O63	3574(3)	−536(7)	1384(7)	5.3
Ru2	3614.6(3)	2853.5(6)	2316.4(6)	2.8	N	3814(4)	2261(8)	870(8)	4.3
Ru3	2765.0(2)	3021.7(6)	4192.3(7)	2.6	C0	3644(3)	2541(8)	4171(10)	2.6
Ru4	3627.3(3)	2192.4(6)	6023.5(6)	2.6	C1	3827(5)	6058(8)	3469(10)	4.3
Ru5	4517.3(2)	2013.7(6)	4099.7(8)	3.1	C2	3999(4)	5256(8)	2518(9)	3.8
Ru6	3419.8(3)	699.7(6)	3868.3(7)	2.8	C3	3599(4)	4771(9)	1610(10)	4.0
O1	3980(5)	1733(10)	0(0)	8.4	C11	3564(4)	5324(8)	5837(8)	3.4
O11	3356(3)	5882(7)	6605(8)	5.4	C12	4655(4)	4836(8)	4975(9)	3.6
O12	5119(3)	5185(8)	5233(8)	5.5	C23	2711(3)	3095(8)	2284(9)	3.4
O23	2348(3)	3233(8)	1547(7)	5.0	C31	1958(3)	2474(9)	4312(10)	3.5
O31	1484(3)	2187(7)	4384(9)	5.7	C32	2511(4)	4659(8)	4381(9)	3.8
O32	2322(3)	5663(6)	4445(9)	5.7	C41	2824(4)	2554(9)	6562(9)	3.8
O41	2425(3)	2657(8)	7170(7)	5.3	C42	4025(5)	3152(9)	7266(10)	4.3
O42	4276(4)	3685(9)	7968(8)	7.3	C43	3678(4)	720(8)	6983(9)	3.6
O43	3721(4)	−141(7)	7591(8)	5.5	C51	5031(5)	2128(11)	5486(11)	5.0
O51	5367(4)	2247(11)	6271(9)	7.6	C52	5044(5)	2757(12)	2967(11)	5.8
O52	5376(4)	3270(12)	2342(11)	9.6	C53	4782(4)	386(11)	3723(14)	5.9
O53	4977(4)	−588(8)	3471(14)	9.4	C61	2622(3)	132(8)	4022(10)	3.8
O61	2161(3)	−324(7)	4060(9)	5.2	C62	3704(4)	−734(8)	4734(10)	4.0
O62	3881(4)	−1568(7)	5215(9)	6.4	C63	3519(3)	−31(9)	2302(10)	3.7

[a] $B_{eq} = 4/3(\sum_i \sum_j B_i j a_{ibj})$.

Table 8. Atomic Coordinates[a] and Equivalent Temperature Factors (Å^2) for $Ru_5C(CO)_{11}(C_3H_5)(NO)_2(NO_2)$ (7)

atom	x	y	z	B_{eq}[b]	atom	x	y	z	B_{eq}[b]
Ru1	2523.3(7)	1227.7(6)	644.1(3)	2.3	N3	65(7)	−432(6)	617(3)	2.6
Ru2	1643.9(7)	985.1(7)	1776.4(3)	2.5	C0	2495(9)	−188(7)	1252(3)	1.9
Ru3	890.2(7)	−1444.1(7)	1298.1(3)	2.4	C1	2597(9)	1536(10)	−307(3)	3.5
Ru4	3336.7(7)	−1434.3(7)	740.7(3)	2.4	C2	2516(10)	2742(9)	−17(5)	4.2
Ru5	3628.2(7)	−979.0(7)	1922.1(3)	2.5	C3	1553(10)	3079(9)	345(4)	4.3
O1	4982(7)	2386(7)	945(3)	5.8	C21	2618(10)	2520(9)	1968(4)	3.6
O2	1746(7)	−2999(7)	2245(3)	5.1	C22	68(10)	1866(10)	1565(4)	4.3
O3	−974(6)	−688(6)	397(3)	4.3	C23	1023(9)	528(9)	2508(5)	4.3
O4	678(5)	546(5)	391(3)	3.0	C31	−702(9)	−1337(10)	1694(4)	4.0
O21	3233(7)	3417(7)	2053(3)	6.4	C32	487(9)	−3117(9)	992(4)	3.2
O22	−859(7)	2374(8)	1426(3)	6.5	C41	3571(9)	−3282(9)	837(4)	4.1
O23	679(8)	248(8)	2946(3)	7.0	C42	5096(9)	−1007(8)	537(4)	3.6
O31	−1700(7)	−1261(8)	1899(3)	7.5	C43	2656(8)	−1565(9)	−3(4)	3.6
O32	213(7)	−4115(6)	835(3)	5.1	C51	5072(9)	234(9)	1894(4)	3.5
O41	3671(8)	−4370(6)	902(3)	5.7	C52	3578(9)	−908(9)	2771(4)	3.8
O42	6129(6)	−671(7)	440(3)	5.9	C53	4833(9)	−2398(9)	1885(4)	3.6
O43	2243(7)	−1628(7)	−442(3)	5.0	H11	329(7)	133(7)	−58(3)	4.1(2.0)
O51	5921(6)	929(7)	1897(3)	6.0	H12	177(8)	122(9)	−38(4)	8.6(3.1)
O52	3519(8)	−917(7)	3209(3)	5.6	H2	314(7)	331(8)	7(3)	4.9(2.3)
O53	5561(7)	−3204(7)	1878(3)	6.2	H31	160(8)	393(8)	65(3)	6.4(2.4)
N1	4005(7)	1899(7)	817(3)	4.1	H32	86(8)	269(8)	45(3)	5.6(2.5)
N2	1978(7)	−2121(7)	1915(3)	2.9					

[a] Fractional ×10^4 for non-hydrogen atoms and ×10^3 for hydrogen atoms. [b] $B_{eq} = 4/3(\sum_i \sum_j B_{ij} a_i b_j)$ for non-hydrogen atoms. Hydrogen atoms were refined isotropically.

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on January 9, 1996 on http://pubs.acs.org | doi: 10.1021/om950570l

chromatographed on silica gel. A green band was eluted with hexane/CH_2Cl_2 (2/1). The eluate was evaporated to dryness, the residue was dissolved in CH_2Cl_2 (10 mL), and the solution was concentrated slowly whereupon green fine crystals of $Ru_5C(CO)_{14}(NO)(NO_2)$ (**3**) precipitated (23% yield). IR (CH_2Cl_2): 2113 m, 2087 s, 2067 vs, 2045 m, 2023 w, 2005 sh, 1601 w, 1524 m, 1468 m cm^{-1}. FAB mass spectrum: *m/z* 985 ($[Ru_5C(CO)_{14}(NO)(NO_2)]^+$, 19), 957 ($[Ru_5C(CO)_{13}(NO)(NO_2)]^+$, 42), 939 ($[Ru_5C(CO)_{14}(NO)]^+$, 42), 901 ($[Ru_5C(CO)_{11}(NO)(NO_2)]^+$, 100%). Anal. Calcd for $C_{15}N_2O_{17}Ru_5$: C, 18.28; N, 2.84. Found: C, 18.37; N, 2.69.

Reaction of $Ru_5C(CO)_{14}(NO)(NO_2)$ (3) with PPh_3. To a solution of **3** (50 mg, 0.05 mmol) in THF (10 mL) was added PPh_3 (200 mg, 0.76 mmol), and the green solution was stirred at room temperature for 48 h. The resulting yellow solution was concentrated to dryness and redissolved in CH_2Cl_2 (1 mL). Workup by column chromatography gave a yellow band which was eluted with hexane/CH_2Cl_2 (2/1). Concentration under reduced pressure and addition of hexane gave yellow-green crystals of $Ru_5C(CO)_{13}(PPh_3)(NO)(NO_2)$ (**4**) (80% yield). IR (CH_2Cl_2): 2101 m, 2063 w, 2056 vs, 2037 s, 2000 w, 1606 w, 1507 m, 1436 w cm^{-1}. FAB mass spectrum: *m/z* 1221 ($[Ru_5C(CO)_{13}(PPh_3)(NO)(NO_2)]^+$, 16), 1193 ($[Ru_5C(CO)_{12}(PPh_3)(NO)(NO_2)]^+$, 9), 1175 ($[Ru_5C(CO)_{13}(PPh_3)(NO)]^+$, 46), 1109 ($[Ru_5C(CO)_9(PPh_3)(NO)(NO_2)]^+$, 100%). Anal. Calcd for $C_{32}H_{15}N_2O_{16}PRu_5$: C, 31.51; H, 1.24; N, 2.30. Found: C, 31.23; H, 1.25; N, 2.34.

Reaction of $[PPN][Ru_6C(CO)_{15}(C_3H_5)]$ (5) with NO. Gaseous NO was bubbled slowly through a CH_2Cl_2 solution (40 mL) of $[PPN][Ru_6C(CO)_{15}(C_3H_5)]$ (**5**) (250 mg, 0.15 mmol). The color of the solution changed gradually from red to red-brown. After 2 h the solution was concentrated and chromatographed on silica gel. A red band was eluted with benzene. The eluate was concentrated and chromatographed again. A red band and an orange band separated on elution with hexane/benzene (2/1). The red eluate was concentrated to dryness, and the residue was crystallized by adding hexane to a CH_2Cl_2 solution to give red crystals of $Ru_6C(CO)_{14}(C_3H_5)(NO)$ (**6**) (30% yield). IR (CH_2Cl_2): 2085 m, 2046 s, 2029 w, 1992 w, 1836 m, 1759 w cm^{-1}. ^1H NMR (C_6D_6, 27 °C): 0.37 (dd, 2H, J_{HH} = 12.5, 2.5 Hz), 1.25 (m, 1H), 3.73 (broad s, 2H). FAB mass spectrum: *m/z* 1082 ($[Ru_6C(CO)_{14}(C_3H_5)(NO)]^+$, 100), 1054 ($[Ru_6C(CO)_{13}(C_3H_5)(NO)]^+$, 15), 1026 ($[Ru_6C(CO)_{12}(C_3H_5)(NO)]^+$, 51), 998 ($[Ru_6C(CO)_{11}(C_3H_5)(NO)]^+$, 50%). Anal. Calcd for $C_{18}H_5NO_{15}Ru_6$: C, 19.99; H, 0.47; N, 1.29. Found: C, 20.14; H, 0.48; N, 1.35. The second orange band was eluted

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on January 9, 1996 on http://pubs.acs.org | doi: 10.1021/om950570l

Table 9. Atomic Coordinates[a] and Equivalent Temperature Factors (Å^2) for $Ru_5C(CO)_{13}(C_3H_5)(NO_2)$ (8)

atom	x	y	z	B_{eq}[b]	atom	x	y	z	B_{eq}[b]
Ru1	6952.3(4)	2565.1(4)	9368.9(8)	3.7	RuB5	7779.0(4)	−411.6(4)	5075.6(9)	4.2
Ru2	6241.1(4)	4012.4(4)	7889.2(9)	4.0	OB1	8728(4)	−1863(5)	9200(8)	7.1
Ru3	7755.8(4)	4452.5(4)	9667.7(8)	3.6	OB2	7529(3)	−1559(3)	7940(7)	4.6
Ru4	7576.7(5)	3919.8*4)	6630.3(9)	4.7	OB11	5341(4)	−1119(5)	3044(9)	8.5
Ru5	8500.1(4)	2998.4(4)	9009.7(10)	4.5	OB21	6900(5)	−3407(4)	7125(9)	7.3
O1	7606(6)	4250(5)	12715(8)	8.7	OB22	5867(4)	−3007(5)	2215(10)	8.7
O2	7202(3)	3252(3)	11383(7)	4.6	OB23	8374(5)	−4155(4)	3896(11)	8.6
O11	6575(5)	1625(4)	6537(8)	6.8	OB31	9526(4)	−3414(4)	7136(10)	8.4
O21	5387(4)	5569(4)	6639(10)	7.9	OB32	9923(5)	−684(5)	7850(10)	8.7
O22	5128(5)	3050(5)	5551(9)	8.4	OB34	9861(4)	−2092(5)	3989(9)	7.5
O23	5292(4)	4035(4)	10266(9)	7.1	OB41	8140(5)	−3033(4)	944(9)	7.9
O31	9380(4)	4790(4)	11875(9)	7.7	OB42	8779(7)	−482(5)	1461(10)	10.9
O32	6692(4)	5877(4)	10340(10)	7.5	OB43	6334(5)	−1094(7)	786(10)	12.0
O34	8416(5)	5526(4)	7841(9)	7.3	OB51	7829(5)	295(4)	8168(8)	7.4
O41	7077(8)	2613(5)	4407(10)	13.4	OB52	9081(5)	577(4)	4533(11)	9.3
O42	6553(5)	5146(5)	4459(9)	8.1	OB53	6375(5)	664(5)	3399(10)	8.4
O43	9128(5)	3979(6)	5569(11)	10.2	NB	8260(4)	−1737(4)	7941(9)	4.6
O51	10133(4)	3608(5)	9086(11)	9.0	CB0	7494(4)	−1526(4)	4797(10)	3.8
O52	8846(6)	1473(5)	7431(14)	12.5	CB1	6108(7)	−482(6)	7290(13)	6.7
O53	9020(4)	2349(5)	12158(10)	9.6	CB2	5560(6)	−1051(7)	6855(14)	7.2
N	7477(5)	3926(4)	11468(9)	5.0	CB3	5871(6)	−1828(6)	7215(13)	6.9
C0	7342(5)	3423(4)	8414(9)	3.5	CB11	5845(5)	−1190(6)	4151(11)	5.3
C1	5975(6)	2187(5)	10311(12)	5.6	CB21	7080(6)	−3111(5)	6205(12)	5.5
C2	6516(6)	1549(5)	10244(12)	5.7	CB22	6435(5)	−2898(6)	3127(12)	5.5
C3	7318(6)	1581(5)	10942(12)	5.6	CB23	8005(6)	−3609(5)	4100(12)	5.8
C11	6727(5)	1986(4)	7662(10)	4.4	CB31	9215(5)	−2837(5)	6726(11)	5.0
C21	5708(5)	5002(6)	7093(12)	5.6	CB32	9492(5)	−1085(6)	7147(12)	6.0
C22	5541(6)	3426(6)	6447(11)	5.7	CB34	9345(5)	−1956(5)	4562(12)	5.2
C23	5640(5)	4007(5)	9349(11)	5.1	CB41	8083(6)	−2509(6)	1704(11)	5.6
C31	8795(5)	4650(5)	11074(11)	4.8	CB42	8480(7)	−893(6)	2019(12)	6.3
C32	7058(6)	5354(5)	10065(12)	5.4	CB43	6941(7)	−1286(7)	1586(12)	7.2
C34	8122(5)	5055(5)	8325(10)	4.5	CB51	7793(6)	48(4)	6956(13)	6.1
C41	7263(9)	3120(7)	5232(12)	8.2	CB52	8597(7)	208(5)	4730(12)	6.0
C42	6933(6)	4696(6)	5283(11)	5.7	CB53	6913(6)	271(5)	4050(12)	5.7
C43	8559(8)	3957(6)	5992(13)	7.3	H11	396(4)	252(4)	1124(8)	4.5(1.8)
C51	9534(6)	3380(5)	9033(14)	6.4	H12	553(5)	227(5)	991(10)	7.8(2.6)
C52	8693(7)	2034(6)	8000(15)	7.5	H2	641(5)	117(4)	943(9)	5.4(2.0)
C53	8817(5)	2580(5)	10948(14)	6.4	H31	756(5)	187(5)	1200(9)	6.2(2.2)
RuB1	6621.6(4)	−134.9(4)	5879.2(9)	4.2	H32	766(5)	127(5)	1066(9)	6.0(2.2)
RuB2	7393.9(4)	−2678.0(4)	4586.9(9)	3.9	HB11	605(5)	5(5)	697(9)	6.0(2.2)
RuB3	8722.9(94)	−1812.4(4)	6023.6(9)	3.7	HB12	636(4)	−43(4)	814(8)	4.9(2.0)
RuB4	7918.7(4)	−1593.2(4)	2930.5(9)	4.3	HB31	565(4)	−213(4)	693(8)	4.0(1.8)

[a] Fractional $\times 10^4$ for non-hydrogen atoms and $\times 10^3$ for hydrogen atoms. [b] $B_{eq} = 4/3(\sum_i \sum_j B_{ij} a_i b_j)$ for non-hydrogen atoms. Hydrogen atoms were refined isotropically.

with benzene and concentrated under reduced pressure to dryness. The residue was dissolved in a minimum amount of CH_2Cl_2, and hexane was added slowly until orange crystals of $Ru_5C(CO)_{11}(C_3H_5)(NO)_2(NO_2)$ (**7**) were formed (11% yield). IR: 2091 m, 2066 w, 2054 s, 2034 m, 1998 w, 1823 w, 1606 w, 1480 w cm^{-1}. ^1H NMR (C_6D_6): 2.78 (d, 2H, $J = 14.2$ Hz), 3.92 (tt, 1H, $J = 14.2$, 8.2 Hz), 5.05 (dd, 2H, $J = 8.2$, 1.3 Hz). FAB mass spectrum: m/z 972 ($[Ru_5C(CO)_{11}(C_3H_5)(NO)_2(NO_2)]^+$, 42), 944 ($[Ru_5C(CO)_{10}(C_3H_5)(NO)_2(NO_2)]^+$, 17), 916 ($[Ru_5C(CO)_9(C_3H_5)(NO)_2(NO_2)]^+$, 35), 888 ($[Ru_5C(CO)_8(C_3H_5)(NO)_2(NO_2)]^+$, 50%). Anal. Calcd for $C_{15}H_5N_3O_{15}Ru_5$: C, 18.52; H, 0.52; N, 4.32. Found: C, 18.61; H, 0.55; N, 4.26.

Reaction of $Ru_6C(CO)_{14}(C_3H_5)(NO)$ (6) with NO. A CH_2Cl_2 solution (10 mL) of **6** (25 mg, 0.023 mmol) was cooled to 0 °C, and 2.5 mL of gaseous NO was bubbled through the solution by a syringe. The reaction took place instantaneously. After 30 min of stirring at 0 °C the solution was concentrated and chromatographed on silica gel. An orange band was eluted with hexane/benzene (4/1), and the eluate was concentrated. Addition of hexange gave orange-red crystals of $Ru_5C(CO)_{13}(C_3H_5)(NO_2)$ (**8**) (37% yield). IR (CH_2Cl_2): 2097 m, 2062 vs, 2050 m, 2024 m, 2000 w, 1957 w cm^{-1}. ^1H NMR (C_6D_6): 2.52 (d, 2H, $J = 12.2$ Hz), 4.30 (m, 1H), 4.43 (d, 2H, $J = 7.3$ Hz). Anal. Calcd for $C_{17}H_5NO_{15}Ru_5$: C, 21.08; H, 0.52; N, 1.45. Found: C, 21.08; H, 0.52; N, 1.41.

Reaction of $[PPN][Ru_6C(CO)_{15}(NO)]$ (2) with Br_2. To a CH_2Cl_2 (2 mL) solution of complex **2** (50 mg, 0.031 mmol) was added slowly a solution (ca. 1 mL) of Br_2/CH_2Cl_2 (10 μL, 0.2 mmol of Br_2 in 2 mL of CH_2Cl_2) under vigorous stirring until no starting complex could be detected any more by IR. The solvent was removed under reduced pressure, and the residue was worked-up by a silica gel column chromatography. The first yellow-green band eluted with hexane/benzene (2/1) was collected and evaporated to dryness. Crystallization from CH_2Cl_2/hexane yielded large green crystals of $Ru_5C(CO)_{14}(NO)Br$ (**9**) (22% yield). IR (CH_2Cl_2): 2111 m, 2085 s, 2065 vs, 2042 m, 2029 sh, 2021 w, 1999 sh, 1526 m. FAB mass spectrum: m/z 1020 ($[Ru_5C(CO)_{14}(NO)Br]^+$, 26), 992 ($[Ru_5C(CO)_{13}(NO)Br]^+$, 24), 964 ($[Ru_5C(CO)_{12}(NO)Br]^+$, 100%). Anal. Calcd for $C_{15}BrNO_{15}Ru_5$: C, 17.67; N, 1.37. Found: C, 17.75; N, 1.40.

Structure Determination. Crystals of **4**, **6**, and **7** were obtained by addition of hexane to CH_2Cl_2 solutions of the compounds followed by slow concentration. Crystals of **8** were grown by addition of hexane to a benzene solution. The single crystals were fixed with Apiezon grease L in glass capillaries under argon. Intensity data were collected by use of an Enraf-Nonius CAD 4 four-circle automated diffractometer with graphite-monochromatized Mo Kα radiation. Crystal data and experimental details are given in Table 5.

Survey of the data set for complex **4** and the systematic extinction indicated a monoclinic class with a space group *Cc* (No. 9) or *C*2/*c* (No. 15). The latter centrosymmetric possibility was strongly indicated by the cell volume (consistent with $Z = 8$) and was confirmed by the successful solution of the structure. Data were corrected for absorption.[22] The analytical form of the scattering factor for the appropriate neutral atom was corrected for both real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersions.[23] The structure was solved by the direct methods program MULTAN.[24] All the non-hydrogen atoms and 14 of the 15 hydrogen atoms were located from subsequent difference Fourier syntheses and refined by the block-diagonal least-squares method[25] with anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms. Positional and thermal parameters are listed in Table 6.

Survey of the data set for complex **6** and the systematic extinction indicated a orthorhombic class with a space group $Pna2_1$ (No. 33). The structure was solved and refined as for **4**. Assignment of the NO ligand was made by the shorter bond length to the ruthenium atom compared with that of CO. Replacement of the nitrogen atom by a carbon atom led to marginally higher residual and GOF values, indicating that the determination was correct. Hydrogen atoms were not located. Final positional and thermal parameters are listed in Table 7.

The data set for complex **7** was not corrected for absorption because deviations of F_o for axial reflections at $\chi \approx 90°$ were within ±3%. The structure was solved and refined as for **4**. All the non-hydrogen and hydrogen atoms were located by subsequent difference Fourier syntheses and refined with anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms. Final positional and thermal parameters are listed in Table 8.

The crystal of **8** belonged to the triclinic space group, and the centrosymmetric space group $P\bar{1}$ was confirmed by the successful refinement of the structure. The crystal contained two independent molecules of **8**, and both molecules appeared to be stereochemically equivalent. Eight allyl-hydrogen atoms, five for one molecule and three for the other one, were located by difference Fourier syntheses and refined as for **4**. Final positional and thermal parameters are listed in Table 9.

Acknowledgment. We are grateful for financial support of this work by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan.

Supporting Information Available: Tables of complete atomic coordinates and thermal parameters and bond lengths and angles (36 pages). Ordering information is given on any current masthead page.

OM950570L

---

(22) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

(23) Cromer, D. T.; Waber, J. T. In *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(24) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declerq, J.-P.; Woolfson, M. M. MULTAN 78, University of York, York, England, 1978.

(25) Sakurai, T.; Kobayashi, K. *Rikagaku Kenkyusho Hokoku* **1979**, *55*, 69.

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on January 9, 1996 on http://pubs.acs.org | doi: 10.1021/om950570l