Inorg. Chem. **1996,** *35,* 7845−7849 **7845**

Syntheses, Structures, and Reactivity of Diruthenium Phosphine Carbonyl Complexes of Nitrites and Nitrates

Kom-Bei Shiu,*,† Luh-Tin Yang,† Shih-Wei Jean,† Chien-Hsing Li,† Ru-Rong Wu,†
Ju-Chun Wang,‡ Lin-Shu Liou,‡ and Michael Y. Chiang§

Departments of Chemistry, National Cheng Kung University, Tainan 701, Taiwan, Republic of China,
Soochow University, Taipei 111, Taiwan, Republic of China, and National Sun Yat-Sen University,
Kaohsiung 804, Taiwan, Republic of China

Received May 16, 1996⊗

A series of diruthenium phosphine carbonyl complexes containing bridging nitro and nitrato groups, $[Ru_2(CO)_4(\mu\text{-}NO_2)_2L_2]$ (**1−4**) and $[Ru_2(CO)_4(\mu\text{-}NO_3)_2L_2]$ (**5−9**), were cleanly prepared from the reactions of $[Ru_2(CO)_4(NCMe)_4L_2][BF_4]_2$ (L = PPh_3, PPh_2(allyl), PPh_2Me, $PPhMe_2$, or PMe_3) with excess $NaNO_2$ or $NaNO_3$ in MeOH. Complexes **1−4** are present in two isomeric forms, **A** and **B**, with a head-to-head orientation of two bridging η^2-(*N*,*O*)-NO_2 groups for form **A** and a head-to-tail arrangement of the groups for form **B**, in an approximate 3:1 ratio, but complexes **5−9** are present in only one isomeric form with an η^2-(*O*,*O*)-NO_3 attachment. Crystal data: **1A**, a = 12.452(2) Å, b = 23.520(3) Å, c = 13.441(2) Å, β = 98.280(1)°, monoclinic $P2_1/n$, Z = 4; **5**, a = 11.737(3) Å, b = 23.496(5) Å, c = 14.629(3) Å, β = 100.34(2)°, monoclinic $P2_1/n$, Z = 4. The five-membered metallacycle $\{Ru_2(ONO)\}$ in **5−9** is more reactive than the four-membered metallacycle $\{Ru_2(NO)\}$ in **1−4**, reflected by the different reactivity of $[Ru_2(CO)_4(\mu\text{-}NO_2)_2(PPh_3)_2]$ (**1**) and $[Ru_2(CO)_4(\mu\text{-}NO_3)_2(PPh_3)_2]$ (**5**) with various reagents to give $[Ru_2(CO)_4(\mu\text{-}I)_2(PPh_3)_2]$ (**10**), $[Ru_2(CO)_4(\mu\text{-}N_3)_2(PPh_3)_2]$ (**11**), and $[Ru_2(CO)_4(\eta^1\text{-}NO_3)_2(\mu\text{-}X)_2(PPh_3)_2]$ (X = Br (**12**), I (**13**)). Crystal data of **13**: a = 31.394(3) Å, b = 9.761(1) Å, c = 18.200(2) Å, β = 118.420(1)°, monoclinic $C2/c$, Z = 4. The intermolecular oxygen transfer from the ligated NO_2 groups in **1** to exogenous PMe_3 is readily observed in MeCN at ambient temperature, apparently forming nitrosyl groups and free $OPMe_3$.

Introduction

The low-valent metal−metal-bonded transition-metal complexes of nitro and nitrato groups, especially those containing reducing phosphine and carbonyl ligands, are of fundamental importance, because the related chemistry can, in principle, help to provide or design suitable metal reagents or catalytic systems to destroy NO_x (x = 1, 2),(1) which are produced in all high-temperature combustion processes by the oxidation of N_2 and fuel-bound nitrogen. However, finding a suitable entry to the complexes remains a great challenge to coordination chemists, in view of the weak coordination ability of nitrate(2) and the facile oxygen transfer from the groups to phosphine and CO.(3) From a serendipitous discovery, we offer here a convenient synthetic approach, leading to a clean and high-yield preparation of a series of such complexes without any accompanying oxygen-transfer product. However, related studies on the transfer and other chemical reactivity are reported. Importantly, the evidence described below indicate that exogenous rather than coordinated phosphines enable the removal of oxygen atoms from coordinated nitro groups.

Results and Discussion

The cation $[Ru_2(CO)_4(NCMe)_6]^{2+}$ has recently been reported to be very versatile, leading to various substitution products such as $[Ru_2(CO)_4(NCMe)_4L_2]^{2+}$ via replacement of two acetonitrile ligands at the axial sites of the complex by phosphines (L).[4a]

---

† National Cheng Kung University.

‡ Soochow University.

§ National Sun Yat-Sen University.

⊗ Abstract published in *Advance ACS Abstracts*, November 15, 1996.

(1) (a) Lee, S. D. *Nitrogen Oxides and Their Effects on Health*; Ann Arbor Science: Michigan, 1980. (b) Armor, J. N. *Environmental Catalysis*; American Chemical Society: Washington, D. C. 1994; p 2.

(2) (a) Addison, C. C. *Coord. Chem. Rev.* **1966**, *1*, 58. (b) Addison, C. C.; Sutton, D. *Prog. Inorg. Chem.* **1967**, *8*, 195. (c) Addison, C. C.; Logan, N.; Wallwork, S. C.; Garner, C. D. *Q. Rev., Chem. Soc.* **1971**, 289. (d) Addison, C. C.; Kilner, M.; Wojcicki, A. *J. Chem. Soc.* **1961**, 4839. (e) Tortorelli, L. J.; Tucker, C. A.; Woods, C.; Bordner, J. *Inorg. Chem.* **1986**, *25*, 3534.

(3) (a) Booth, G.; Chatt, J. *J. Chem. Soc.* **1962**, 2099. (b) Hieber, W.; Beutner, H. *Z. Anorg. Allg. Chem.* **1963**, *320*, 101. (c) Grundy, K. R.; Laing, K. R.; Roper, W. R. *J. Chem. Soc. D* **1970**, 1500. (d) Nesmeyanov, A. N.; Anisimov, K. N.; Kolobova, N. E.; Krasnoslobodskaya, L. L. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1970**, 807; *Izv. Akad. Nauk SSSR, Ser. Khim.* **1970**, 860. (e) Johnson, B. F. G.; Bhaduri, S. *J. Chem. Soc., Chem. Commun.* **1973**, 650. (f) Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 3325. (g) Bhaduri, S.; Johnson, B. F. G.; Savory, C. J.; Segal, J. A.; Walter, R. H. *J. Chem. Soc., Chem. Commun.* **1974**, 809. (h) Efraty, A.; Arneri, R.; Sikora, J. *J. Organomet. Chem.* **1975**, *91*, 65. (i) Ugo, R.; Bhaduri, S.; Johnson, B. F. G.; Khair, A.; Pickard, A.; Benn-Taarit, Y. *J. Chem. Soc., Chem. Commun.* **1976**, 694. (j) Bhaduri, S.; Johnson, B. F. G.; Matheson, T. W. *J. Chem. Soc., Dalton Trans.* **1977**, 561. (k) Keene, F. R.; Salmon, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 4821. (l) Tovrog, B. S.; Diamond, S. E.; Mares, F. *J. Am. Chem. Soc.* **1979**, *101*, 270. (m) Doughty, D. T.; Gordon, G.; Stewart, R. P., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 2645. (n) Feltham, R. D.; Kriege, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 5064. (o) Dubrawski, J.; Kriege-Simmondsen, J. C.; Feltham, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 2089. (p) Abruna, H. D.; Walsh, J. L; Meyer, T. J.; Murray, R. W. *J. Am. Chem. Soc.* **1980**, *102*, 3272. (q) Doughty, D. T.; Stewart, R. P., Jr.; Gordon, G. *J. Am. Chem. Soc.* **1981**, *103*, 3388. (r) Stevens, R. E.; Yanta, T. J.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1981**, *103*, 4891. (s) Oberdorfer, F.; Balbach, B.; Ziegler, L. *Z. Naturforsch.* **1982**, *37b*, 157. (t) Kriege-Simmondsen, J. C.; Elbaze, G.; Dartiguenave, M.; Feltham, R. D.; Dartiguenave, J. *Inorg. Chem.* **1982**, *21*, 230. (u) Stevens, R. E.; Gladfelter, W. L. *Inorg. Chem.* **1983**, *22*, 2034. (v) Andrews, M. A.; Chang, T. C.-T.; Cheng, C. W. F. *Organometallics* **1985**, *4*, 268. (w) Johnson, B. F. G.; Sieker, A.; Blake, A. J.; Winpenny, E. P. *J. Chem. Soc., Chem. Commun.* **1993**, 1345. (x) Johnson, B. F. G.; Sieker, A.; Blake, A. J.; Winpenny, R. E. P. *J. Organomet. Chem.* **1994**, *475*, 193.

S0020-1669(96)00530-7 CCC: $12.00

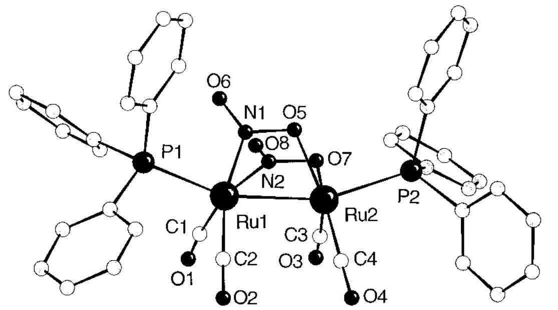
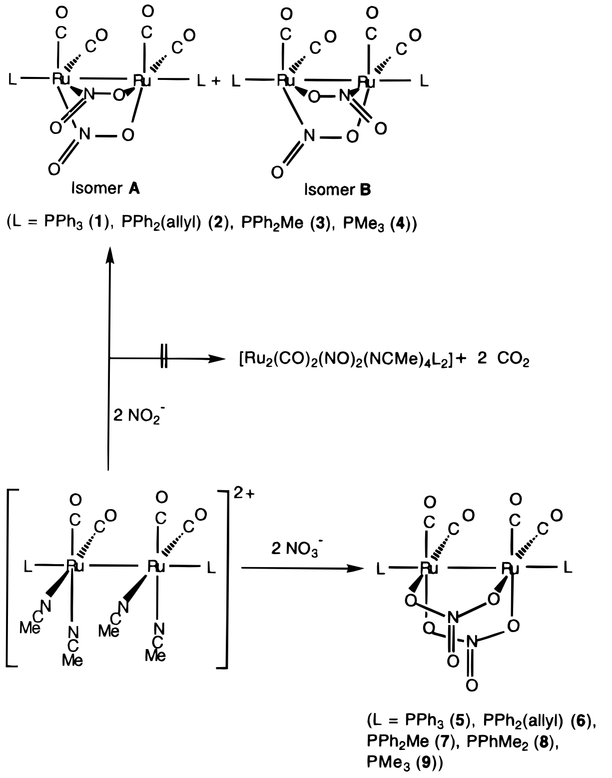


Figure 1. CAMERON[6] plot of **1A**. Selected bond lengths (Å) and angles (deg) and absolute values of torsional angles (deg): Ru(1)−Ru(2) 2.665(2), Ru(1)−P(1) 2.436(4), Ru(1)−N(1) 2.103(12), Ru(1)−N(2) 2.111(10), Ru(1)−C(1) 1.902(13), Ru(1)−C(2) 1.860(15), Ru(2)−P(2) 2.416(4), Ru(2)−O(5) 2.146(9), Ru(2)−O(7) 2.131(9), Ru(2)−C(3) 1.882(14), Ru(2)−C(4) 1.851(18), N(1)−O(5) 1.311(11), N(1)−O(6) 1.226(12), N(2)−O(7) 1.274(12), N(2)−O(8) 1.196(12), Ru(1)−N(1)−O(5) 114.5(8), Ru(1)−N(1)−O(6) 131.9(9), O(5)−N(1)−O(6) 113.2(11), Ru(1)−N(2)−O(7) 113.4(8), Ru(1)−N(2)−O(8) 129.6(9), O(7)−N(2)−O(8) 116.8(10), Ru(2)−O(5)−N(1) 103.0(7), Ru(2)−O(7)−N(2) 105.1(7), Ru(1)−Ru(2)−P(2) 159.8(1), Ru(2)−Ru(1)−P(1) 158.8(1), N(1)−Ru(1)−Ru(2)−O(5) 1.8(4), N(2)−Ru(1)−Ru(2)−O(7) 1.2(4), C(2)−Ru(1)−Ru(2)−C(4) 2.5(6), C(1)−Ru(1)−Ru(2)−C(3) 1.3(6).

With the seemingly firm attachment of the equatorial acetonitrile ligands in $[Ru_2(CO)_4(NCMe)_4(PPh_3)_2]^{2+}$, Hieber's[3b] or Gladfelter's[3u] approach was followed to prepare neutral nitrosyl complexes $[Ru_2(CO)_2(NO)_2(NCMe)_4(PPh_3)_2]$ with expected formation of an oxygen-transfer product, CO_2, by heating a reaction mixture of $[Ru_2(CO)_4(NCMe)_4(PPh_3)_2][BF_4]_2$ and an excess amount of $Na^+NO_2^-$ or $PPN^+NO_2^-$ (PPN^+ = bis(triphenylphosphine)nitrogen(1+)) in MeOH. To our surprise, we did not obtain the nitrosyl complex, but something different. There are two ^{15}N NMR singlets at 108 and 113 ppm observed for this product, which are not typical chemical shifts for the presence of a linear NO group.[5] Later, a combination of the elemental analyses, NMR, and crystal structure results revealed that the product contains two bridging η^2-(*N*,*O*)-NO_2 groups and consists of two isomers, **A** and **B**, in either a head-to-head geometry of the two groups (**1A**, cf. Figure 1) or a head-to-tail structure (**1B**). Very similar NMR spectra were obtained by dissolving either the product or the single crystals of **1A** in acetone-d_6,[7] indicating that the two isomers are present in an equilibrium mixture. The synthetic method for **1** can be employed generally to produce not only other nitro complexes with different phosphines ligated $[Ru_2(CO)_4(\mu\text{-}NO_2)_2L_2]$ (L = PPh_2(allyl) (**2**); PPh_2Me (**3**); PMe_3 (**4**)) but also the nitrato complexes $[Ru_2(CO)_4(\mu\text{-}NO_3)_2L_2]$ (L = PPh_3 (**5**); PPh_2(allyl) (**6**); PPh_2Me (**7**); $PPhMe_2$ (**8**); PMe_3 (**9**)) in 85−93% yield (Scheme 1). Probably, ligation of the bulkier and softer phosphines at the axial sites with the soft Ru(I) atoms may help to weaken the bonding interactions between the soft metal atoms and the hard equatorial MeCN ligands in $[Ru_2(CO)_4(NCMe)_4L_2]^{2+}$, facilitating replacement of these ligands even with weak σ-donors such as nitrate and formation of **5**−**9**. Of course, we cannot exclude a thermodynamic boost from the insolubility of **1**−**9** in the solvent we used. Like **1**, the nitro complexes **2**−**4** are also a mixture of two isomers in an approximate ratio of **A**:**B** = 3:1, as indicated by the four carbonyl ^{13}C NMR singlets at δ 205.64 (**1A** or **1B**), 205.61 (**1A** or **1B**), 205.38 (**1A**), and 205.00 (**1B**), and the five $^{31}P\{^1H\}$ NMR signals with one AB quartet assigned to isomer **A** and one singlet assigned to isomer **B** of **1**−**4**. Attempts to separate the two isomers failed, probably due to the fact that the two isomers of **2**−**4** are also in equilibrium in solution. On the contrary, each nitrato complex of **5**−**9** is present as only one isomeric form, displaying one $^{31}P\{^1H\}$ NMR singlet and being confirmed by the crystal structure of **5** (Figure 2). It contains two η^2-(*O*,*O*)-NO_3 bridges.

Scheme 1



The Ru−Ru distance of 2.665(2) Å in **1A** is significantly shorter than that of 2.695(2) Å in **5**, but both distances are still in the range 2.558−2.873 Å for other singly Ru(I)−Ru(I) bonded complexes with ligation of PPh_3 ligands.[4,8] The two PPh_3 groups are not collinear with the Ru−Ru bond, but bent away from the carbonyl groups toward nitro groups in **1A** and nitrato groups in **5** with angles ∠Ru−Ru−P of 158.8(1) and 159.8(1)° in **1A** and those of 166.1(1) and 167.7(1)° in **5**, probably reflecting that CO is a stronger π-acid than a nitro or nitrato group in the complexes. The two phosphorus atoms in either structure are not coplanar with two {Ru_2(NO)} planes in **1A** or two {Ru_2(ONO)} planes in **5**, but are clipped by the two planes. The larger angles ∠Ru−Ru−P found in **5**, relative to those in **1A**, are attributed to the fact that the space occupied by two nitrato groups is larger than that for the nitro groups.

It has been well established in the literature that a four-membered ring such as cyclobutane and a five-membered ring such as cyclopentane prefer to be puckered in order to reduce the inherent torsional strain in planar forms.[9] The five-membered metallacycle {Ru_2(ONO)} in **5** is indeed slightly

---

(4) (a) Klemperer, W. G.; Bianxia, Z. *Inorg. Chem.* **1993**, *32*, 5821. (b) Shiu, K.-B.; Li, C.-H.; Chan, T.-J.; Peng, S.-M.; Cheng, M.-C.; Wang, S.-L.; Liao, F.-L.; Chiang, M. Y. *Organometallics* **1995**, *14*, 524.

(5) Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyls*, Oxford University Press: New York, 1992; p 60.

(6) Pearce, L. J.; Watkin, D. J.; Prout, C. K. *CAMERON*; Chemical Crystallography Laboratory, Oxford University, U.K., 1995.

(7) One reviewer kindly drew our attention to the NMR experiment by dissolving single crystals of **1A**.

(8) (a) Sherlock, S. J.; Cowie, M.; Singleton, E.; Steyn, M. M. de V. *J. Organomet. Chem.* **1989**, *361*, 353. (b) Andren, P. L.; Cabeza, J. A.; Riera, V.; Robert, F.; Jeannin, Y. *J. Organomet. Chem.* **1989**, *372*, C15. (c) Garcia-Granda, S.; Obeso-Rosete, R.; Gonzalez, J. M. R.; Anillo, A. *Acta Crystallogr.* **1990**, *C46*, 2043. (d) Shiu, K.-B.; Peng, S.-M.; Cheng, M.-C. *J. Organomet. Chem.* **1993**, *452*, 143.

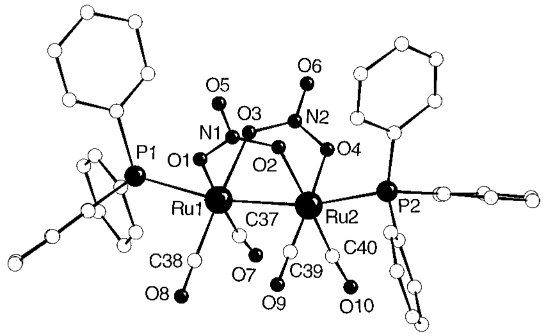
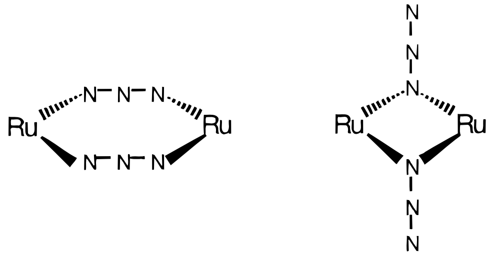


Figure 2. CAMERON plot of **5**. Selected bond lengths (Å) and angles (deg), and absolute values of torsional angles (deg): Ru(1)−Ru(2) 2.695(2), Ru(1)−P(1) 2.457(4), Ru(1)−O(1) 2.13(1), Ru(1)−O(3) 2.14(1), Ru(1)−C(37) 1.78(2), Ru(1)−C(38) 1.88(2), Ru(2)−P(2) 2.437(4), Ru(2)−O(2) 2.07(1), Ru(2)−O(4) 2.13(1), Ru(2)−C(39) 1.80(2), Ru(2)−C(40) 1.80(2), N(1)−O(1) 1.23(2), N(1)−O(2) 1.27(2), N(1)−O(5) 1.26(2), N(2)−O(3) 1.27(2), N(2)−O(4) 1.28(2), N(2)−O(6) 1.20(2), Ru(2)−Ru(1)−P(1) 166.1(1), Ru(1)−Ru(2)−P(2) 167.7(1), Ru(1)−O(1)−N(1) 121(1), Ru(2)−O(2)−N(1) 126(1), Ru(1)−O(3)−N(2) 125(1), Ru(2)−O(4)−N(2) 122(1), O(1)−N(1)−O(2) 121(1), O(3)−N(2)−O(4) 120(1), O(3)−Ru(1)−Ru(2)−O(4) 15.8(5), O(1)−Ru(1)−Ru(2)−O(2) 17.7(6), C(38)−Ru(1)−Ru(2)−C(39) 17.1(8), C(37)−Ru(1)−Ru(2)−C(40) 16.1(8).

skewed with the twist angle (κ)[10] of 16.7° around the Ru−Ru bond, but the four-membered metallacycle {$Ru_2(NO)$} in **1A** is nearly planar, with $\kappa = 1.7°$. Though the Ru−O distances in **1A** and **5** are very similar within the experimental errors and the Ru−N distances of 2.103(12) and 2.111(10) Å in **1A** are also within a reported range of 2.10(1)−2.208(5) Å between a Ru(I) atom and an N(sp^2) atom,[11] the close planarity of the four-membered metallacycle {$Ru_2(NO)$} in **1A** can be ascribed to the presence of back-donation from a filled antibonding orbtial, π^* or δ^*, on the d^7−d^7 Ru_2 system[12] to a vacant π^* orbital of NO_2^-.[13] Except for the apparently longer N−O distances found in **1A** (d(N(2)−O(7)) = 1.274(12) Å and d(N(1)−O(5)) = 1.311(11) Å), compared with the value of 1.236(14) Å found in $NaNO_2$,[14] the back-donation argument appears to gain other support in the different chemical reactivity of **1** and **5** toward a strong nucleophile such as iodide. It converts **5** into [$Ru_2(CO)_4(\mu\text{-}I)_2(PPh_3)_2$] (**10**) nearly quantitatively at ambient temperature, but this temperature cannot drive any reaction between iodide anions and **1**. When the reaction mixture of **1** and excess NaI was heated under reflux at 82 °C in MeCN, **10** was formed with many other products, as reflected in a ^{31}P NMR spectrum. Synthesis of **10**, with one or two mononuclear products, was reported previously from cluster fragmentation of [$Ru_2(CO)_4(\mu\text{-}Cl)_2(\mu\text{-}Fe(CO)_4)(PPh_3)_2$][15] and [$Ru_3(CO)_9(PPh_3)_3$][16] by reacting with I^- and I_2, respectively. Apparently the conversion from **5** into **10** represents a more economical synthetic pathway than any fragmentation approach. With the back-donation, the Ru_2 system gains some metal−metal "multiple" bonding character,[12] explaining why the observed Ru−Ru bond length in **1A** is significantly shorter than that in **5**. Similar "multiple" metal−metal bonding is probably present as well in other Ru(I) complexes such as [$Ru_2(CO)_4(NCMe)_6$]$^{2+}$, reflecting as the observed strong *trans*-labilizing effect of the Ru−Ru bond in the easier replacement of axial- than equatorial-MeCN ligands.[4a]

One typical oxygen-transfer experiment from ligated NO_2 groups to exogenous phosphines has been carried out for **1**. As shown by the solution IR and ^{31}P NMR spectra, compound **1** is stable in MeCN at ambient temperature, but upon addition of PMe_3, a singlet at δ 36.0 assigned to free $OPMe_3$ and seven other singlets at 31.6, 26.0, 1.7, 1.6, −4.5, −8.6, and −8.8 appeared readily within 2 h. The presence of $OPMe_3$ was further confirmed by comparison with the authentic sample and checked with blank experiments. After the oxygen transfer, the nitro groups seem to form nitrosyl groups, as indicated by the appearance of a stretching band of medium intensity at 1682 cm^{-1} with other bands at 2062 w, 1985 m, 1970 m, 1935 w, and 1883 s cm^{-1} in an IR spectrum. However, the assignment is still tentative in the absence of ^{15}N labeling data. If the oxygen transfer is an orbital-controlled process, a basic orbital consideration[13b] would suggest that the exogenous phosphine may attack the central nitrogen atom of the nitro group prior to oxygen transfer to give $OPMe_3$.

Analogous to the preparation of **10** from **5**, the azido complex [$Ru_2(CO)_4(\mu\text{-}N_3)_2(PPh_3)_2$] (**11**) was also formed readily from **5** by reacting with an excess amount of NaN_3 at ambient temperature. The typical strong−medium−strong pattern of the carbonyl stretching bands in an IR spectrum and only one ^{31}P singlet in an NMR spectrum observed for **11** suggested that it should have a structure similar to that of **10**, having a single Ru(I)−Ru(I) bond, two bridging azides, two axial phosphines, and four equatorial carbonyls in a sawhorse arrangement. Azide can form either an end-to-end or an end-on bridge to connect two different metal atoms in a dinuclear compound.[17] However, only the latter type of bridge is believed to be possible in **11**, for being compatible with the presence of a metal−metal single bond with d(Ru−Ru) < 2.873 Å.[4]



Some reactions of **5** with electrophiles were carried out. It was found that 1 equiv of X_2 can convert **5** into a yellow compound with an empirical formula of [$Ru(CO)_2(NO_3)X(PPh_3)$] (X = Br (**12**), I (**13**)), showing only two carbonyl stretching bands in solution and in the solid state. The X-ray structure of **13** (Figure 3) then helped to assure the dimeric nature with two bridging halides and two monodentate nitrates η^1-(O)-NO_3, but without a metal−metal bonding interaction (d(Ru−Ru) = 4.102(1) Å) (Scheme 2). From Figures 2 and 3, the nitrate donors appear to favor the positions *trans* to the acceptor groups (carbonyl), probably reflecting that the successful synthesis of any complex containing a poor σ-donor such

---

(9) Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; Wiley: New York, 1994; p 755.

(10) (a) Cotton, F. A.; Shiu, K.-B. *Gazz. Chim. Ital.* **1985**, *115*, 705. (b) Barnes, C. M.; Bohle, D. S.; Madsen, S. K. *Inorg. Chem.* **1994**, *33*, 6411.

(11) (a) Cabeza, J. A.; Riera, V.; Pellinghelli, M. A.; Tiripicchio, A. *J. Organomet. Chem.* **1989**, *376*, C23. (b) Pellinghelli, M. A.; Tiripicchio, A.; Cabeza, J. A.; Oro, L. A. *J. Chem. Soc., Dalton Trans.* **1990**, 1509. (c) Langenbahn, M.; Stoeckli-Evans, H.; Süss-Fink, G. *J. Organomet. Chem.* **1990**, *397*, 347.

(12) Shiu, K.-B.; Guo, W.-N.; Peng, S.-M.; Cheng, M.-C. *Inorg. Chem.* **1994**, *33*, 3010.

(13) (a) Gimarc, B. M. *Molecular Structure and Bonding*, Academic Press: New York, 1979; p 158. (b) Pfeiffer, G. V.; Allen, L. C. *J. Chem. Phys.* **1969**, *51*, 190.

(14) Carpenter, G. B. *Acta Crystallogr.* **1955**, *8*, 852.

(15) Jones, D. F.; Dixneuf, P. H.; Benoit, A.; Le Marouille, J.-Y. *Inorg. Chem.* **1983**, *22*, 29.

(16) Kramer, G.; Poe, A.; Amer, S. *Inorg. Chem.* **1981**, *20*, 1362.

(17) Ribas, J.; Monfort, M.; Ghosh, B. K.; Cortes, R.; Solans, X.; Font-Bardia, M. *Inorg. Chem.* **1996**, *35*, 864.

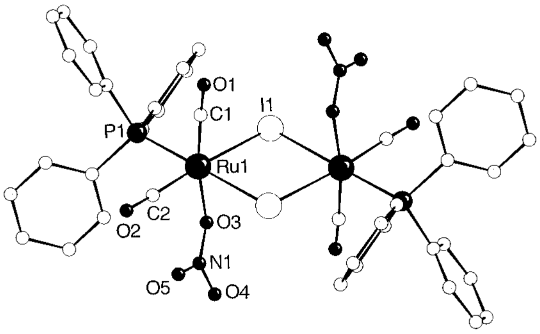
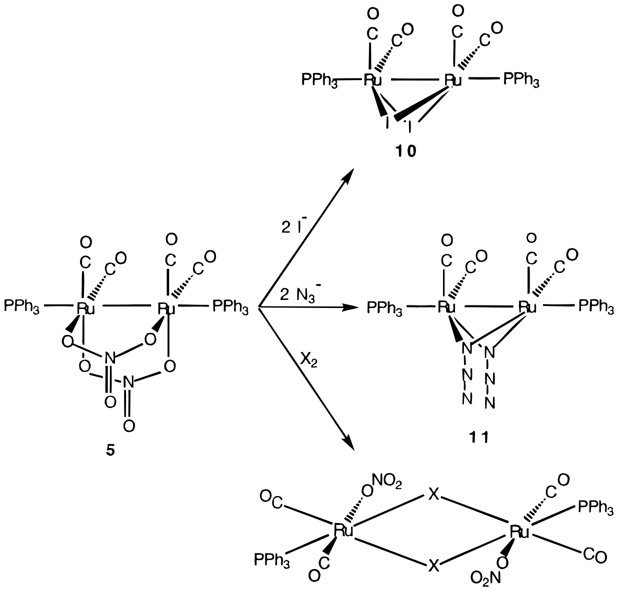


Figure 3. CAMERON plot of **13**. Selected bond lengths (Å) and angles (deg): Ru(1)−I(1) 2.766(1), Ru(1)−P(1) 2.372(3), Ru(1a)−I(1) 2.761(1), Ru(1)−O(3) 2.142(6), Ru(1)−C(1) 1.861(9), Ru(1)−C(2) 1.896(7), Ru(1)−O(3) 2.142(6), O(3)−N(1) 1.233(9), N(1)−O(4) 1.211(12), N(1)−O(5) 1.223(11), C(1)−O(1) 1.116(12), C(2)−O(2) 1.112(10), Ru(1)−I(1)−Ru(1a) 95.8(1), I(1)−Ru(1)−P(1) 179.4(1), C(1)−Ru(1)−O(3) 170.8(3), O(3)−N(1)−O(4) 117.6(8), O(3)−N(1)−O(5) 123.9(8), O(4)−N(1)−O(5) 118.5(8), I(1)−Ru(1)−C(1) 88.1(4), I(1)−Ru(1)−C(2) 90.1(3).

Scheme 2



(X = Br (**12**), I(**13**))

as a nitrate anion relies on the presence of a metal fragment with an enhanced σ-acidity. A net positive charge or the presence of π-acceptor ligands such as NO or CO in the fragment is essential.

Conclusions

This study has established that the cationic complex $[Ru_2(CO)_4(NCMe)_4L_2]^{2+}$ has weakly-coordinated equatorial MeCN ligands, which can be replaced by nitrite and nitrate anions to give nitro and nitrato complexes, **1**−**9**, readily without any accompanying oxygen-transfer products (Scheme 1). Structures and reactivity of both nitro and nitrato complexes are compared. Facile oxygen transfer can occur intermolecularly from ligated nitro groups to exogenous PMe_3 in MeCN at ambient temperature, apparently giving nitrosyl groups and free $OPMe_3$. The five-membered metallacycle, formed by two Ru atoms and the bridging nitrato group in **5**−**9**, is fragile, as shown by the reactions of **5** with nucleophilic and electrophilic reagents to afford **10**−**13** (Scheme 2).

Experimental Section

General Comments. All solvents were dried and purified by standard methods (ethers, paraffins, and arenes from potassium with benzophenone as indicator; halocarbons and acetonitrile from CaH_2 and alcohols from the corresponding alkoxide) and were freshly distilled under nitrogen immediately before use. All reactions and manipulations were carried out in standard Schlenk ware, connected to a switchable double manifold providing vacuum and nitrogen. Reagents and phosphines were used as supplied by either Aldrich or Strem. ^1H and ^{31}P NMR spectra were measured on a Bruker AM-200 (^1H, 200 MHz) or AMC-400 or a Varian Unity Plus-400 (^1H, 400 MHz; ^{31}P, 162 MHz) NMR spectrometer. ^1H chemical shifts (δ in ppm, J in Hz) are defined as positive downfield relative to internal $MeSi_4$ (TMS) or the deuterated solvent, while ^{31}P chemical shifts are defined as positive downfield relative to external 85% H_3PO_4. The IR spectra were recorded on a Hitachi Model 270-30 or Bio-Rad FTS 175 instrument. The following abbreviations were used: s, strong; m, medium; w, weak; s, singlet; d, doublet; t, triplet; br, broad unresolved signal. Microanalyses were carried out by the staff of the Microanalytical Service of the Department of Chemistry, National Cheng Kung University.

Synthesis of $[Ru_2(CO)_4(\mu,\eta^2\text{-}NO_2)_2L_2]$ (L = PPh_3 (1), $PPh_2(allyl)$ (2), PPh_2Me (3), PMe_3 (4)). The preparations of **1**−**4** are similar to each other. A typical procedure for **3** is described below. The phosphine complex $[Ru_2(CO)_4(NCMe)_4(PPh_2Me)_2][BF_4]_2$ (0.127 g, 0.121 mmol)[4b] was dissolved in 20 mL of MeOH. $Na^+NO_2^-$ (0.059 g, 0.86 mmol) was then added to the mixture. This mixture was heated under reflux for 1 h, forming an orange-yellow precipitate. The solid was collected. Recrystallization from CH_2Cl_2 and MeOH afforded pure product (0.089 g) in a yield of 91%. For **1**: orange-yellow. Anal. Calcd for $C_{40}H_{30}N_2O_8P_2Ru_2$: C, 51.62; H, 3.25; N, 3.01. Found: C, 51.35; H, 3.37; N, 3.02. IR (CH_2Cl_2): ν_{CO} 2048 s, 2008 m, 1986 s, 1954 m cm^{-1}. $^{31}P\{^1H\}$ NMR (162 MHz, acetone-d_6): δ 19.08 (d, 1 P, J = 79 Hz), 17.42 (d, 1 P, J = 79 Hz) for **1A**; 16.95 (s, 2 P) for **1B**. ^{15}N NMR (40.5 MHz, CH_2Cl_2): δ 113 (s, 2 N) for **1A**; 108 (s, 2 N) for **1B**. For **2**: orange-yellow. Anal. Calcd for $C_{34}H_{30}N_2O_8P_2Ru_2$: C, 47.56; H, 3.52; N, 3.26. Found: C, 47.48; H, 3.57; N, 3.36. IR (CH_2Cl_2): ν_{CO} 2044 s, 2000 m, 1984 s, 1950 m cm^{-1}. $^{31}P\{^1H\}$ NMR (162 MHz, acetone-d_6): δ 16.61 (d, 1 P, J = 79 Hz), 14.64 (d, 1 P, J = 79 Hz) for **2A**; 14.87 (s, 2 P) for **2B**. For **3**. Anal. Calcd for $C_{30}H_{26}N_2O_8P_2Ru_2$: C, 44.67; H, 3.25; N, 3.47. Found: C, 44.68; H, 3.27; N, 3.42. IR (CH_2Cl_2): ν_{CO} 2044 s, 2000 m, 1982 s, 1952 m cm^{-1}. $^{31}P\{^1H\}$ NMR (162 MHz, acetone-d_6): δ 7.04 (d, 1 P, J = 76 Hz), 4.74 (d, 1 P, J = 76 Hz) for **3A**; 5.12 (s, 2 P) for **3B**. For **4**: orange-red. Anal. Calcd for $C_{10}H_{18}N_2O_8P_2Ru_2$: C, 20.38; H, 3.08; N, 4.75. Found: C, 20.45; H, 3.25; N, 4.71. IR (CH_2Cl_2): ν_{CO} 2040 s, 1994 m, 1974 s, 1944 m cm^{-1}. $^{31}P\{^1H\}$ NMR (162 MHz, acetone-d_6): δ −9.05 (d, 1 P, J = 71 Hz), −16.54 (d, 1 P, J = 71 Hz) for **4A**; −12.43 (s, 2 P) for **4B**.

Synthesis of $[Ru_2(CO)_4(\mu,\eta^2\text{-}NO_3)_2L_2]$ (L = PPh_3 (5), $PPh_2(allyl)$ (6), PPh_2Me (7), $PPhMe_2$ (8), PMe_3 (9)). In a 100-mL Schlenk flask were added 0.089 mmol of $[Ru_2(CO)_4(NCMe)_4(PR_3)_2][BF_4]_2$,[4b] 0.032 g of $Na^+NO_3^-$ (0.376 mmol), and 15 mL of MeOH at room temperature. The mixture was then heated at 65 °C for 1 h and cooled to room temperature, forming orange precipitate, which was collected on a medium frit. Recrystallization from a mixture of CH_2Cl_2 and MeOH afforded pure products. For **5**: orange-yellow. Anal. Calcd for $C_{40}H_{30}N_2O_{10}P_2Ru_2$: C, 49.90; H, 3.14; N, 2.91. Found: C, 49.95; H, 3.13; N, 2.76. ^1H NMR (25 °C, 200 MHz, acetone-d_6): δ 7.48 (m, 30 H). $^{31}P\{^1H\}$ NMR (25 °C, 162 MHz, acetone-d_6): δ 16.8 (s, 2 P). IR (CH_2Cl_2): ν_{CO} 2044 s, 2000 m, 1976 s cm^{-1}. For **6**: orange-yellow. Anal. Calcd for $C_{34}H_{30}N_2O_{10}P_2Ru_2$: C, 45.85; H, 3.39; N, 3.14. Found: C, 45.69; H, 3.52; N, 3.04. ^1H NMR (25 °C, 200 MHz, $CDCl_3$): δ 3.31 (m, 4 H), 4.97 (m, 4 H), 5.58 (m, 2 H), 7.54 (m, 20 H). $^{31}P\{^1H\}$ NMR (25 °C, 162 MHz, $CDCl_3$): δ 13.9 (s, 2 P). IR (CH_2Cl_2): ν_{CO} 2044 s, 2000 m, 1972 s cm^{-1}. For **7**: orange-yellow. Anal. Calcd for $C_{30}H_{26}N_2O_{10}P_2Ru_2$: C, 42.97; H, 3.12; N, 3.34. Found: C, 42.76; H, 3.16; N, 3.28. ^1H NMR (25 °C, 200 MHz, $CDCl_3$): δ 2.06 (t, 6 H, J = 2.0), 7.40 (m, 20 H). $^{31}P\{^1H\}$ NMR (25 °C, 162 MHz, $CDCl_3$): δ 4.8 (s, 2 P). IR (CH_2Cl_2): ν_{CO} 2040 s, 1998 m, 1972 s cm^{-1}. For **8**: orange-yellow. Anal. Calcd for $C_{20}H_{22}N_2O_{10}P_2Ru_2$: C, 33.62; H, 3.10; N, 3.29. Found: C, 33.44; H, 3.16; N, 3.27. ^1H NMR (25 °C, 200 MHz, $CDCl_3$): δ 1.94 (m, 12 H), 7.52 (m, 10 H). $^{31}P\{^1H\}$ NMR (25 °C, 162 MHz, $CDCl_3$): δ −5.2 (s, 2 P). IR (CH_2Cl_2): ν_{CO} 2040 s, 1994 m, 1970 s cm^{-1}. For **9**: orange-yellow. Anal. Calcd for $C_{10}H_{18}N_2O_{10}P_2Ru_2$: C, 20.35; H, 3.07; N,

Table 1. Crystal Data for **1A**, **5**, and **13**

compd	**1A**	**5**	**13**
formula	$C_{40}H_{30}N_2O_8P_2Ru_2$	$C_{40}H_{30}N_2O_{10}P_2Ru_2$	$C_{40}H_{36}I_2N_2O_{13}P_2Ru_2$
fw	930.7	962.77	1270.6
space group	monoclinic, $P2_1/n$ (No. 14)	monoclinic, $P2_1/n$ (No. 14)	monoclinic, $C2/c$ (No. 15)
a, Å	12.452(2)	11.737(3)	31.394(3)
b, Å	23.520(3)	23.496(5)	9.761(1)
c, Å	13.441(2)	14.629(3)	18.200(2)
β, deg	98.280(1)	100.34(2)	118.420(1)
V, Å^3	3895.3(13)	3968(1)	4904.7(9)
Z	4	4	4
d_{calcd}, g cm^{-3}	1.587	1.611	1.721
λ(Mo Kα), Å	0.710 73	0.710 69	0.710 73
μ(Mo Kα), cm^{-1}	9.12	9.02	19.88
temp, K	298	296	298
R^a, $R_w{}^a$	0.063, 0.068	0.065, 0.082	0.042, 0.055

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

4.75. Found: C, 20.24; H, 3.09; N, 4.76. ^{1}H NMR (25 °C, 200 MHz, $CDCl_3$): δ 1.61 (t, 18 H, $J = 4.0$). $^{31}P\{^1H\}$ NMR (25 °C, 162 MHz, $CDCl_3$): δ −10.5 (s, 2 P). IR (CH_2Cl_2): υ_{CO} 2040 s, 1992 m, 1966 s cm^{-1}.

Synthesis of $[Ru_2(CO)_4(\mu\text{-}I)_2(PPh_3)_2]$ (10). To a stirred solution of **5** (0.097 g, 0.101 mmol) dissolved in 15 mL of MeCN was added 0.039 g of NaI (0.26 mmol) at room temperature. An orange-red precipitate gradually formed. After 1 h, the solvent was removed under vacuum, giving a red solid. Recrystallization from CH_2Cl_2/MeOH gave 0.105 g of **10** (96%). Anal. Calcd for $C_{40}H_{30}I_2O_4P_2Ru_2$: C, 43.97; H, 2.77. Found: C, 43.77; H, 2.75. ^{1}H NMR (25 °C, 200 MHz, acetone-d_6): δ 7.58 (m, 30 H). $^{31}P\{^1H\}$ NMR (25 °C, 162 MHz, acetone-d_6): δ 30.6 (s, 2 P). IR (CH_2Cl_2): υ_{CO} 2032 s, 1992 m, 1962 s cm^{-1}.

Synthesis of $[Ru_2(CO)_4(\mu\text{-}N_3)_2(PPh_3)_2]$ (11). This yellow compound was prepared in 95% yield by a procedure analogous to that of **10**, from **5** and NaN_3. Anal. Calcd for $C_{40}H_{30}N_6O_4P_2Ru_2$: C, 51.86; H, 3.20; N, 8.92. Found: C, 52.06; H, 3.28; N, 9.11. ^{1}H NMR (25 °C, 200 MHz, acetone-d_6): δ 7.54 (m, 30 H). $^{31}P\{^1H\}$ NMR (25 °C, 162 MHz, acetone-d_6): δ 26.4 (s, 2 P). IR (CH_2Cl_2): υ_{CO} 2020 s, 1990 m, 1950 s cm^{-1}.

Synthesis of $[Ru_2(CO)_4(\eta^1\text{-}NO_3)_2(\mu\text{-}X)_2(PPh_3)_2]$ (X = Br (12), I (13)). To a stirred solution of **1** (0.107 g, 0.114 mmol) dissolved in 15 mL of CH_2Cl_2 was added dropwise an I_2 solution containing 0.029 g of I_2 (0.114 mmol) and 10 mL of CH_2Cl_2 at room temperature. After 10 min, the solvent was removed under vacuum. Recrystallization from CH_2Cl_2/hexane gave 0.131 g of orange-yellow solid (**13**) (94%). Anal. Calcd for $C_{40}H_{30}I_2N_2O_{10}P_2Ru_2$: C, 39.49; H, 2.49; N, 2.30. Found: C, 39.37; H, 2.53; N, 2.31. $^{31}P\{^1H\}$ NMR (162 MHz, acetone-d_6): δ 39.6 (s, 2 P). IR: υ_{CO} 2072 s, 2020 s in CH_2Cl_2 and 2068 s, 2012 s cm^{-1} in a KBr disk. Compound **12** was obtained similarly in a yield of 90%. Anal. Calcd for $C_{40}H_{30}Br_2N_2O_{10}P_2Ru_2$: C, 42.80; H, 2.69; N, 2.50. Found: C, 42.82; H, 2.71; N, 2.53. $^{31}P\{^1H\}$ NMR (162 MHz, acetone-d_6): δ 33.7 (s, 2 P). IR: υ_{CO} 2076 s, 2024 s in CH_2Cl_2 and 2068 s, 2016 s cm^{-1} in a KBr disk.

Single-Crystal X-ray Diffraction Studies of 1A, 5, and 13. Suitable single crystals were grown from CH_2Cl_2/hexane or CH_2Cl_2/Et_2O at room temperature and chosen for the single-crystal structure determination. The X-ray diffraction data were measured on a four-circle diffractometer. Intensities of three standard reflections were monitored every hour or every 50 reflections throughout the data measurement. The variation was less than 2%.

For **1** and **13**, the structures were solved by direct methods and refined by a full-matrix least-squares procedure using SHELXTL-PLUS.[18] For **5**, the structure was solved by direct methods and refined by a full-matrix least-squares procedure using TEXSAN.[19]

Both $C2/c$ and Cc space groups were tried for **13**. The index of averaging equivalents is $R_{int} = 0.0251$ for $C2/c$ and $R_{int} = 0.0000$ for Cc. The reasons for choosing $C2/c$ as the final model are as follows: (1) the mean value of $|E^2 - 1|$ is 0.936, which suggests that the centrosymmetric space group is a better choice; (2) under the Cc space group, the least-squares refinements have a convergence problem; (3) the carbon atoms on the two carbonyl groups, which were symmetry related under the $C2/c$ space group, could not be refined anisotropically for the Cc space group; a non-positively-defined atom resulted for these two carbon atoms; and (4) the large displacement parameters of few carbon atoms on a phenyl ring did not get better when the space group changed from $C2/c$ to Cc.

The R_{int} value is 0.0293 for structure **1A** and 0.0214 for structure **5**. That an extinction correction was not applied in the final model for the two structures is explained as follows. For **1A**, the application of the correction gave an insignificant final value $\chi = 0.000\,03(4)$, and the trend of F_c greater than F_o was not observed. For **5**, the application of the correction resulted in a physically meaningless (negative) value.

Structure **13** contains a crystallographically imposed inversion center, and 0.5 molecule and 1.5 H_2O were found in each asymmetric unit. Hydrogen positions for water molecules were not located. The essential details of single-crystal data measurement are given in Table 1.

Acknowledgment. We are grateful to the National Science Council of Republic of China (Contract NSC85-2113-M006-012) for financial support. The CAMERON figures of **1A**, **5**, and **13** were kindly drawn by John F. Saunders.

Supporting Information Available: Tables of detailed crystal data, the atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms, complete bond lengths and angles, anisotropic displacement parameters, and hydrogen atomic coordinates for **1A**, **5**, and **13** (13 pages). Ordering information is given on any current masthead page.

IC960530P

---

(18) (a) Siemens Analytical X-ray Instruments Inc., Karlsruhe, Germany, 1991. (b) *International Tables for X-Ray Crystallography*; Kluwer Academic Publishers: Dordrecht, Holland, 1974; Vol. 4.

(19) (a) Crystal Structural Analysis Package, Molecular Structure Corp., TX, 1985, 1992. (b) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; The Kynoch Press: Birmingham, U.K., 1974; Vol. 4.