Synthesis and Reactivity of the Formally Unsaturated Diruthenium Diphosphazane-bridged Species $[Ru_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i)

John S. Field, Raymond J. Haines,* Jörg Sundermeyer and Stephen F. Woollam

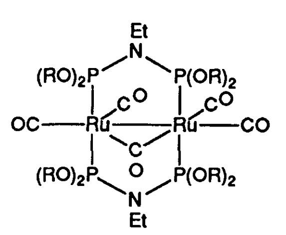
Unit of Metal Cluster Chemistry, Department of Chemistry, University of Natal, PO Box 375, Pietermaritzburg, Republic of South Africa

Thermolysis of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ or $[Ru_2H_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i) under appropriate reaction conditions affords the formally unsaturated species $[Ru_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$, which reacts spontaneously at room temperature with various substrates; the crystal structure of $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ as well as that of $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ is reported.

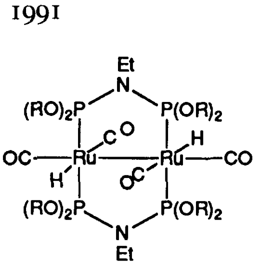
The prime objective in the design of dinuclear complexes that function as homogeneous catalysts for various organic reactions or that can be employed under mild conditions as precursors in the synthesis of generally inaccessible products, is the development of systems that readily give rise to, or are themselves, formally coordinatively unsaturated species. Some typical unsaturated dinuclear carbonyl and diphosphorus ligand-bridged carbonyl derivatives, which have been reported include $[M_2(\mu\text{-}H)_2(CO)_8]^{2-}$ (M = Cr, Mo or W),[1] $[Re_2(\mu\text{-}H)_2(CO)_8]$,[2] $[M_2'(\mu\text{-}H)_2(CO)_6\{\mu\text{-}(EtO)_2POP(OEt)_2\}]$,[3,4] $[M_2'(\mu\text{-}H)_2(CO)_6(Ph_2PCH_2PPh_2)]$ (M′ = Mn or Re)[4,5] and $[Mn_2(\mu\text{-}H)_2(CO)_4(\mu\text{-}Ph_2PCH_2PPh_2)_2]$.[6] On the other hand, $[Mn_2(\mu\text{-}\eta^2\text{-}CO)(CO)_4(\mu\text{-}Ph_2PCH_2PPh_2)_2]$[7,8] represents an example of a related dinuclear compound, which can be formally converted to an unsaturated species; in this case through the bridging carbonyl reverting from a four- to a two-electron ligand. We now report the synthesis of an unsaturated dinuclear diphosphazane-bridged derivative of ruthenium, $[Ru_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i), which in contrast to the unsaturated species above does not contain an $M_2(\mu_2\text{-}H)_2$ fragment, and which exhibits high reactivity.

Passage of dihydrogen through a toluene solution of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (**1**; R = Pr^i)[9] at 80 °C was found to lead to a colour change from yellow to red, which reverted to yellow on cooling to room temperature and from which yellow crystals of the dihydride $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (**2**; R = Pr^i) (see below) could be isolated in high yield. It was assumed that the red colour could be attributed to an intermediate in the formation of the dihydride being present in solution and that this intermediate is a decarbonylation product of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$. Indeed, the heating of a toluene solution of this pentacarbonyl derivative at 80 °C was again found to lead to a change in the colour of the solution from yellow to red but on the basis of a $^{31}P\{^1H\}$ NMR spectral study the extent of the presumed decarbonylation was found to be minimal. However, passage of a stream of argon through a toluene solution of this pentacarbonyl derivative at 80 °C led to the formation of an intense purple product, which on crystallization from toluene at −25 °C, afforded purple-black crystals of a compound characterized as $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (**3**; R = Pr^i).[†]

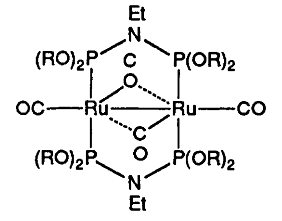
[†] The synthesis of $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ can also be achieved by pyrolysis of either solid $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ or solid $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ under vacuum at 80 °C or by passage of argon through a toluene solution of $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ at 80 °C.



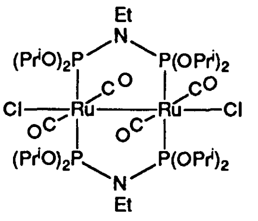
1



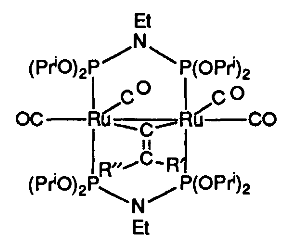
2



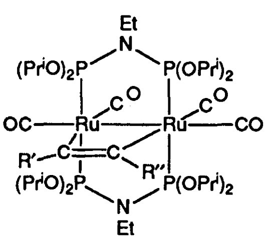
3



4



5



6

The molecular structure of this compound was established X-ray crystallographically and is illustrated in Fig. 1.‡ The presence of only four carbonyl groups is confirmed with two of them being shown to occupy axial sites and to be essentially collinear. The other two carbonyls are best described as semi-bridging and are related to each other through a centre of inversion [Ru–C(2) = 1.92(1); Ru′–C(2) = 2.43(1)Å]. The Ru–C(2)–O(2) bond angle of 153.5(9)° can only be interpreted in terms of these equatorial carbonyl groups not functioning as four-electron donors§ and on this basis, with no unusual short contact distances being apparent, the compound must be considered as being formally coordinatively unsaturated. The ruthenium–ruthenium distance of 2.763(1) Å is marginally shorter than that for $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ [2.801(2) Å][9] and certainly longer than that expected for a Ru–Ru double bond such that the presence of a Ru–Ru double bond can be disregarded. An alternative possibility is that this compound occurs as a diradical and consistent with this, as established for the photolysis product of $[Re_2(CO)_8(\mu\text{-}Ph_2PCH_2PPh_2)]$,[10,11] it reacts spontaneously with CCl_4 to afford a dichloro product *viz.* $[Ru_2Cl_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ **4**.[12] However, no signal could be observed in the ESR spectrum of this compound indicating that if it does exist as a diradical the electrons must be weakly antiferromagnetically coupled.

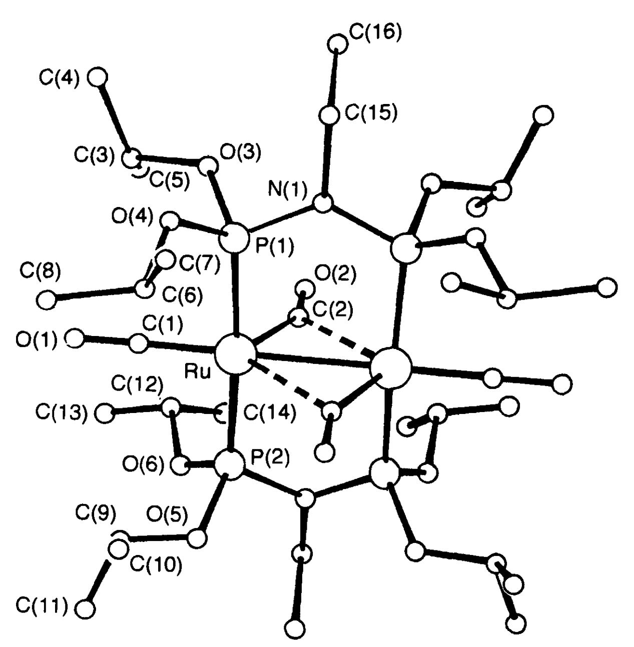


Fig. 1 The stereochemistry of $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ showing the atom labelling scheme. Relevant interatomic distances and angles: Ru–Ru′ 2.763(1), Ru–P(1) 2.312(2), Ru–P(2) 2.317(2), Ru–C(2) 1.92(1), Ru′–C(2) 2.43(1) Å; Ru–C(2)–O(2) 153.5(9)°.

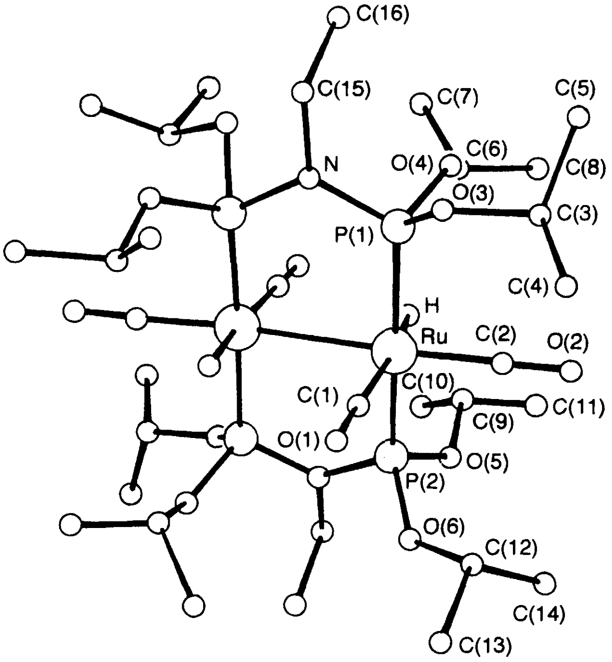


Fig. 2 The stereochemistry of $[Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ showing the atom labelling scheme. Relevant interatomic distances: Ru–Ru′ 2.911(1), Ru–P(1) 2.297(1), Ru–P(2) 2.288(1), Ru–H 1.72(6) Å.

Not surprisingly, $[Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ is highly reactive and reacts spontaneously with both nucleophiles and electrophiles such as carbon monoxide, alkynes, sulphur dioxide, stannous chloride, carbon tetrachloride, dihydrogen, dioxygen, halogens, protons and silver(I) salts. Addition of CO resulted in the formation of the parent pentacarbonyl derivative $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (**1**; R = Pr^i)[9] while that of alkynes led to the formation of vinylidene-bridged products of the type

---

‡ *Crystal data*: $C_{32}H_{66}N_2O_{12}P_4Ru_2$, M = 997.0, monoclinic, space group $P2_1/n$ (No. 14), a = 13.238(2), b = 9.872(3), c = 17.486(1) Å, β = 95.58(1)°, U = 2274.4 Å^3, D_c = 1.46 g cm^{-3}, Z = 2, Mo-Kα radiation, λ = 0.71069 Å, μ = 8.30 cm^{-1}. Nonius CAD4 diffractometer, 2593 unique reflections with $I > 3\sigma(I)$ in the range $3 \leq \theta \leq 23°$. Structure solved using direct methods and successive Fourier maps and refined to R = 0.075 (165 parameters). Tables of atomic coordinates, interatomic distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ A disordered structure in which each equatorial carbonyl functions alternatively as either a four-electron bridging group or a two-electron terminal ligand was eliminated on the basis of the low temperature factors for their carbon and oxygen atoms.

$[\mathrm{Ru_2\{\mu\text{-}\eta^1\text{-}C{=}C(R')R''\}(CO)_4\{\mu\text{-}Pr^iO)_2PN(Et)P(OPr^i)_2\}_2}]$ **5**[13] and/or alkendiyl-bridged derivatives of formula $[\mathrm{Ru_2\{\mu\text{-}\sigma^2\text{-}R'C{=}CR''\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2}]$ **6**[13] depending on the nature of the alkyne.

The product of the reaction involving dihydrogen was characterized as the dihydride $[\mathrm{Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2}]$ (**2**; R = $\mathrm{Pr^i}$) best synthesized as described above. The molecular structure of this compound was also established by X-ray crystallography and is illustrated in Fig. 2.¶ The salient feature of the structure is that the hydrogen atoms are terminal and occupy equatorial sites. The compound adopts a near eclipsed configuration [P(1)–Ru–Ru′–P(2)′ = 8.6(1)°] with a Ru–Ru distance [2.911(1) Å] slightly longer than that for the tetramethoxydiphosphazane parent species $[\mathrm{Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2}]$ (see above).[9]

$[\mathrm{Ru_2H_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2}]$ is also highly reactive affording vinylidene-bridged and/or alkenediyl-bridged species on reaction with alkynes and the parent compound $[\mathrm{Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2}]$ (**1**; R = $\mathrm{Pr^i}$) on reaction with carbon monoxide. Although not to the same extent as $[\mathrm{Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2}]$ (**3**; R = $\mathrm{Pr^i}$), it is susceptible to attack by oxygen affording a product, which has still to be fully characterized. It can be dehydrogenated to $[\mathrm{Ru_2(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2}]$ under thermal conditions and in fact, as described above, the thermolysis of this dihydride is an appropriate alternative method for the synthesis of the tetracarbonyl derivative.

Thermolysis of $[\mathrm{Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2}]$ (**1**; R = Me) or $[\mathrm{Ru_2H_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2}]$ (**2**; R = Me) also leads to the formation of an unsaturated product *viz.* $[\mathrm{Ru_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2}]$ (**3**; R = Me) but the reaction is slower and the yield is less.

The authors express their sincere thanks to the Foundation for Research Development and the University of Natal for financial support.

Received, 22nd May, 1991; Com. 1/02416G

References

1 J. T. Lin, G. P. Hagen and J. E. Ellis, *J. Am. Chem. Soc.*, 1983, **105**, 2296.

2 M. J. Bennet, W. A. G. Graham, J. K. Hayano and W. L. Hutcheon, *J. Am. Chem. Soc.*, 1972, **94**, 6232.

3 V. Riera, M. A. Ruiz, A. Tiripicchio and M. Tiripicchio-Camellini, *J. Chem. Soc., Chem. Commun.*, 1985, 1505.

4 F. J. Garcia-Alonso, M. Garcia-Sanz, V. Riera, M. A. Ruiz, A. Tiripicchio and M. Tiripicchio-Camellini, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1167.

5 M. J. Mays, D. W. Prest and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1980, 171; *J. Chem. Soc., Dalton Trans.*, 1982, 2021.

6 H. C. Aspinall and A. J. Deeming, *J. Chem. Soc., Chem. Commun.*, 1983, 838.

7 R. Colton and C. J. Commons, *Aust. J. Chem.*, 1975, **28**, 1673.

8 C. J. Commons and B. J. Hoskins, *Aust. J. Chem.*, 1975, **28**, 1663.

9 G. de Leeuw, J. S. Field, R. J. Haines, B. McCulloch, E. Meintjies, C. Monberg, G. M. Olivier, P. Ramdial, C. N. Sampson, B. Sigwarth, N. D. Steen and K. G. Moodley, *J. Organomet. Chem.*, 1984, **275**, 99.

10 K.-W. Lee, W. T. Pennington, A. W. Cordes and T. L. Brown, *J. Am. Chem. Soc.*, 1985, **107**, 631.

11 K.-W. Lee, J. M. Hanckel and T. L. Brown, *J. Am. Chem. Soc.*, 1986, **108**, 2266.

12 J. S. Field, R. J. Haines, C. N. Sampson and J. Sundermeyer, *J. Organomet. Chem.*, 1986, **310**, C42.

13 J. S. Field, R. J. Haines, J. Sundermeyer and S. F. Woollam, *S. Afr. J. Chem.*, in press.

¶ *Crystal data*: $\mathrm{C_{32}H_{68}N_2O_{12}P_4Ru_2}$, $M = 999.0$, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.432(1)$, $b = 11.729(2)$, $c = 12.075(2)$ Å, $\alpha = 105.722(14)$, $\beta = 103.648(11)$, $\gamma = 115.114(13)°$, $U = 1178.74$ Å^3, $D_c = 1.41$ g cm^{-3}, $Z = 1$, Mo-Kα radiation, $\lambda = 0.71069$ Å, $\mu = 8.05$ cm^{-1}. Nonius CAD4 diffractometer, 3081 unique reflections with $I > 3\sigma(I)$ in the range $3 \leqslant \theta \leqslant 23°$. Structure solved from a Patterson synthesis and successive Fourier maps and refined to $R = 0.036$ (240 parameters). Tables of atomic coordinates, interatomic distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors Issue No. 1.