# Formation of a N–C Bond between Co-ordinated α-Di-imine and a Novel Diketene Fragment; *X*-Ray Crystal Structure of $\{\overline{Ru_2(CO)_5[Pr^iN\overset{..}{-}C(H)\overset{..}{-}(H)C{-}N(Pr^i)C(O)CH_2C(O)CH_2}]\}$ containing an $\eta^3$-Aza-allyl to Ru Bonded Moiety

**Louis H. Polm,**[a] **Gerard van Koten,**[a] **Kees Vrieze,***[a] **Casper H. Stam,**[b] **and Wil C. J. van Tunen**[b]
[a]*Laboratorium voor Anorganische Chemie*
[b]*Laboratorium voor Kristallografie, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands*

The reaction of $H_2C{=}C{=}O$ with $[Ru_2(CO)_6(R\text{-dab})]$ [R-dab = $RN{=}C(H){-}(H)C{=}NR$; R = $Pr^i$, $C_6H_{11}$] at room temperature in heptane afforded in virtually quantitative yields $\{\overline{Ru_2(CO)_5[RNC(H)C(H)N(R)C(O)CH_2C(O)CH_2}]\}$; the *X*-ray crystal structure for the compound with R = $Pr^i$ shows two novel structural features, (i), a head-to-tail bonded diketene moiety incorporated in a six membered $\overline{RuCH_2C(O)CH_2C(O)N}(R)$ ring and (ii), an R-dab ligand converted into an $\eta^3$-bonded amino-aza-allyl ligand.

In the area of activation of organic substrates by cluster molecules the interest in our laboratory is focussed on the properties of the very versatile α-di-imine [$RN{=}C(H){-}(H)C{=}NR$ = R-dab] ligand. When co-ordinated, for example as a σ-N,σ-N′,$\eta^2$-C=N 6e donor ligand in $[Ru_2(CO)_6(R\text{-dab})]$ (**1**) the R-dab ligand may be involved in C–C coupling reactions of the $\eta^2$-C=N bonded C-atom with substrates such as R-dab itself,[1,2] carbodi-imides RN=C=NR,[3] sulphines $R_2C{=}S{=}O$,[3] and alkynes.[4] Up till now we had not been able to activate the imine N atoms for N–C coupling reactions in the complexes $[Ru_2(CO)_6(R\text{-dab})]$. In our search for suitable organic substrates our attention was directed to ketenes $R_2C{=}C{=}O$, since only fairly recently it has been reported that ketenes may co-ordinate either through the C=C bond as in

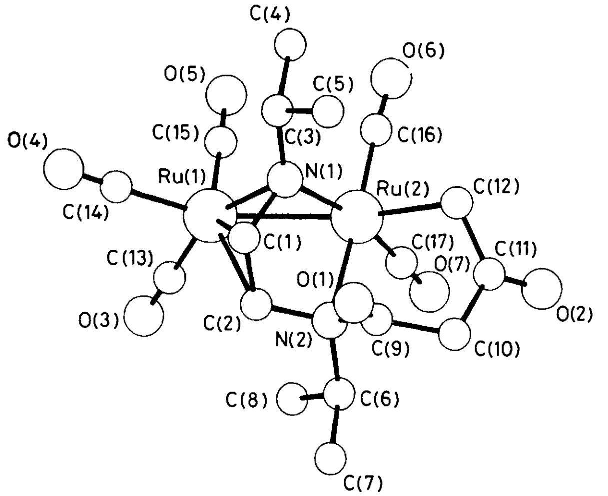

**Figure 1.** Molecular structure of $\{Ru_2(CO)_5[Pr^iNC(H)C(H)N(Pr^i)C(O)CH_2C(O)CH_2]\}$ (2), Important bond lengths are: Ru(1)–Ru(2), 2.752(1); Ru(1)–N(1), 2.178(5); Ru(1)–C(1), 2.159(6); Ru(1)–C(2), 2.285(6); Ru(2)–N(1), 2.154(4); Ru(2)–N(2), 2.215(4); Ru(2)–C(12), 2.200(6); C(11)–C(12), 1.438(9); C(10)–C(11), 1.535(8); C(9)–C(10), 1.492(8); N(2)–C(9), 1.477(8); N(2)–C(6), 1.552(7); N(1)–C(3), 1.484(7); C(9)–O(1), 1.203(6); C(11)–O(2), 1.225(8) Å.

$[Pt(PPh_3)_2(Ph_2C{=}C{=}O)]$,[5] $[Ni(PPh_3)_2(Ph_2C{=}C{=}O)]$,[6] and $[Mn(C_5H_5)(CO)_2(Ph_2C{=}C{=}O)]$,[7] or through the C=O bond as in $[Ti(C_5H_5)_2(Ph_2C{=}C{=}O)]$[8] and $[V(C_5H_5)_2(Ph_2C{=}C{=}O)]$.[9] Also, as shown, *e.g.* by Deeming and coworkers,[10] ketene itself when bonded to $Os_3$ clusters may extensively rearrange on the cluster, in processes that may involve rupture of C–C and C–H bonds. In view of these recent observations it was expected that a varied chemistry may be found in reactions of ketenes with metal–R-dab complexes. Treatment of $[Ru_2(CO)_6(R\text{-}dab)]$ (1) (R = $Pr^i$, $C_6H_{11}$, but not R = $Bu^t$) in heptane solution at room temp. with gaseous ketene, formed by pyrolysis of acetone,[11] afforded in almost quantitative yields the yellow coloured $\{Ru_2(CO)_5[RNC(H)C(H)N(R)C(O)CH_2C(O)CH_2]\}$ [R = $Pr^i$ (2), R = $C_6H_{11}$ (3)]. In the case of R = $Bu^t$ no reaction occurred under the conditions used.

$$[Ru_2(CO)_6(R\text{-}dab)]$$
(1)

$$\{Ru_2(CO)_5[RNC(H)C(H)N(R)C(O)CH_2C(O)CH_2]\}$$
(2), R = $Pr^i$
(3), R = $C_6H_{11}$

The molecular structure of (2) has been established by *X*-ray diffraction (see Figure 1).†

*Crystal data* for (2): $C_{17}H_{20}N_2O_7Ru_2$; $M$ = 566.49, monoclinic, space group $P2_1/a$, $a$ = 13.4462(8), $b$ = 18.5488(2), $c$ = 8.3238(4) Å, $\beta$ = 103.23(1)°, $Z$ = 4. A total of 3230 intensities were measured on a Nonius CAD4 diffractometer using graphite monochromated Cu-$K_\alpha$ radiation; 34 were below the $2.5\sigma(I)$ level and were treated as unobserved. An absorption correction was applied ($\mu$ = 127.7 $cm^{-1}$; transmission factor from 0.14 to 0.43).

The structure was solved by a Patterson minimum function based on the position of the 8 Ru atoms in the unit cell which were derived from an $E^2$ Patterson synthesis. Refinement proceeded by block diagonal least-squares calculations, anisotropic for Ru, C, N, and O and isotropic for H atoms, the positions of which were derived from a $\Delta F$ synthesis. The final $R$ value was 0.039. A weighting scheme $w = 1/(5.1 + F_o + 0.008F_o^2)$ was employed and the anomalous scattering of Ru was taken into account.

The framework of this bimetallic complex consists of an $Ru_2(CO)_5$ unit [Ru–Ru 2.752(1) Å] with terminal groups spanned by an 8e terdentate donor ligand which is formed *via* N–C coupling of the co-ordinated 6e donor $Pr^i$-dab group to a non-cyclic diketene group. In the di-imine moiety of this terdentate ligand one may distinguish an RN(1)C(1)C(2) unit which is $\eta^3$-co-ordinated to Ru(1) with N(1)–C(1) and C(1)–C(2) bond lengths of 1.396(7) and 1.405(8) Å respectively indicating extensive electron delocalization.‡ The $\eta^3$-aza-allyl group is asymmetrically linked to Ru(1) as shown by the Ru(1)–N(1), Ru(1)–C(1), and Ru(1)–C(2) bond distances of 2.178(5), 2.159(6), and 2.285(6) Å respectively, which is probably mainly due to steric constraints in the terdentate ring. The other part of the ligand is a six-membered $RuCH_2C(O)CH_2C(O)N(Pr^i)$-ring composed of a head-to-tail coupled diketene group to which the Ru(2)–N(2) moiety is added in a 1,4 manner. The bond lengths in the ring are as expected for single C–C bonds.

The i.r. spectra of *e.g.* (2) show the presence of terminal carbonyl groups (in $CH_2Cl_2$ solution) and further, two CO stretching bands at 1732 (w,br.) and 1638 (w,br.) $cm^{-1}$ which are typical for a ketonic CO group and a carbonyl group inserted between a N- and a C-atom, respectively.[14]

The $^1H$ and $^{13}C$ n.m.r. spectra in $CDCl_3$ solutions of (2) and (3) are in accordance with a molecular structure as shown in Figure 1. The $^1H$ n.m.r. signals of H(1) and H(2) appear at $\delta_H$ 7.36 and 3.64 respectively with a coupling constant of 2.2 Hz.§ The C(1) and C(2) signals appear at $\delta_C$ 104.4 and 57.1 p.p.m. respectively. These values may be compared with those of $\{MnFe(CO)_6[Pr^iNC(H)C(H)N(H)Pr^i]\}$[12] which appear for the H atoms at $\delta$ 6.69 and 3.40 respectively ($J$ 2 Hz) and for the corresponding carbon atoms at $\delta_C$ 101.1 and 58.0 p.p.m. respectively. The CO groups absorb around $\delta_C$ 200.6 p.p.m., while the ketonic CO and the $-N-CO-CH_2-$ appear at $\delta_C$ 193.9 and 172.5 p.p.m. respectively for (2). The four methyl groups of the two isopropyl substituents can be observed as four doublets which agrees with the dissymmetry of the molecular structure in the solid.

Considering the molecular structure of (2) there are several novel features. Firstly, in the reaction of ketene with $[Ru_2(CO)_6(R\text{-}dab)]$ the ketene molecules have dimerised head-to-tail which for ketene itself is unprecedented, since diketene is 1,2-cyclodimerised head-to-head and tail-to-tail.[15] Secondly, the coupling of the open diketene unit to one of the N atoms of the di-imine moiety instead of the hitherto

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† Atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ These distances may be compared with the similar bond lengths of 1.38(2) and 1.39(2) Å in $\{MnFe(CO)_6[Pr^iNC(H)C(H)N(H)Pr^i]\}$[12] and of 1.455(7) and 1.332(6) Å in $\{MoI(C_5H_5)[C(NMe_2)C(Me)NMe]\}$.[13] In the last case arguments were put forward to regard the trihapto arrangement as an imino-dimethylaminocarbene ligand. The carbene formulation is clearly not applicable in complex (2).

§ H(1) and H(2) are linked to C(1) and C(2) respectively in Figure 1.

observed C–C coupling[1–4] is indeed unusual. Thirdly it is of interest to point out that this is the first time that it has been shown that the R-dab ligand may be converted to an $\eta^3$-bonded amino-aza-allyl ligand. Finally, the reaction mechanism resulting in the formation of (**2**) and (**3**) is of interest, since reaction of diketene with $[Ru_2(CO)_6(R\text{-dab})]$ does not produce such complexes. It is interesting to note that $[Ru_2(CO)_6(Bu^t\text{-dab})]$ does not react with gaseous ketene which may suggest that the reaction is controlled to an important degree by steric factors.

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