

and hydrogen; and they believed this stability was due to the radical being immobilized at an inaccessible site on the alumina surface.

Several attempts were made to stabilize the methyl radical on the surface of the Type 3A zeolite in order to compare its reaction with oxygen to that of the encapsulated radical. A thoroughly degassed sample (*ca.* 10^{-3} Pa, 350 °C) was equilibrated with CH₄ at 77 K, evacuated to 0.02 Pa and sealed off. The sample, while still immersed in liquid nitrogen, was irradiated as before (⁶⁰Co *ca.* 1 Mrad dose) but only the signal associated with the blank zeolite was observed. This is probably due to the small exterior surface of the 3A zeolite sample and the small amount of methane which can be adsorbed. By comparison, the 4A zeolite used by the previous workers^{5,6} to stabilize Me radicals allows the methane molecule to penetrate the pores freely and thus presents a much greater surface for adsorption.

Very recently, Griffith *et al.*¹⁹ have reported that they have observed very weak methyl e.s.r. signals in naturally occurring lepispheric cherts after heating. They have explained this signal as arising from organic species trapped in molecular sized holes in the silica substrate. The presence of such a signal, albeit weak, at ambient temperatures is very promising as it would suggest that with suitable modifications of the zeolite structure, systems might be developed in which the methyl radical is encapsulated at room temperature, and yet could be released by heating the zeolite to higher temperatures. Such 'bottled' methyl radicals could obviously have considerable potential utility as polymerization initiators.

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Formation of a N–C Bond between Co-ordinated α -Di-imine and a Novel Diketene Fragment; X-Ray Crystal Structure of

$\{\text{Ru}_2(\text{CO})_5[\text{Pr}^i\text{N}=\text{C}(\text{H})-\text{C}(\text{H})-\text{N}(\text{Pr}^i)\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CH}_2]\}$ containing an η^3 -Aza-allyl to Ru Bonded Moiety

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The reaction of H₂C=C=O with [Ru₂(CO)₆(R-dab)] [R-dab = RN=C(H)–(H)C=NR; R = Prⁱ, C₆H₁₁] at room temperature in heptane afforded in virtually quantitative yields $\{\text{Ru}_2(\text{CO})_5[\text{RNC}(\text{H})\text{C}(\text{H})\text{N}(\text{R})\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CH}_2]\}$; the X-ray crystal structure for the compound with R = Prⁱ shows two novel structural features, (i), a head-to-tail bonded diketene moiety incorporated in a six membered RuCH₂C(O)CH₂C(O)N(R) ring and (ii), an R-dab ligand converted into an η^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', η^2 -C=N 6e donor ligand in [Ru₂(CO)₆(R-dab)] (1) the R-dab ligand may be involved in C–C coupling reactions of the η^2 -C=N bonded C-atom with substrates such

as R-dab itself,^{1,2} carbodi-imides RN=C=NR,³ sulphines R₂C=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 [Ru₂(CO)₆(R-dab)]. In our search for suitable organic substrates our attention was directed to ketenes R₂C=C=O, since only fairly recently it has been reported that ketenes may co-ordinate either through the C=C bond as in

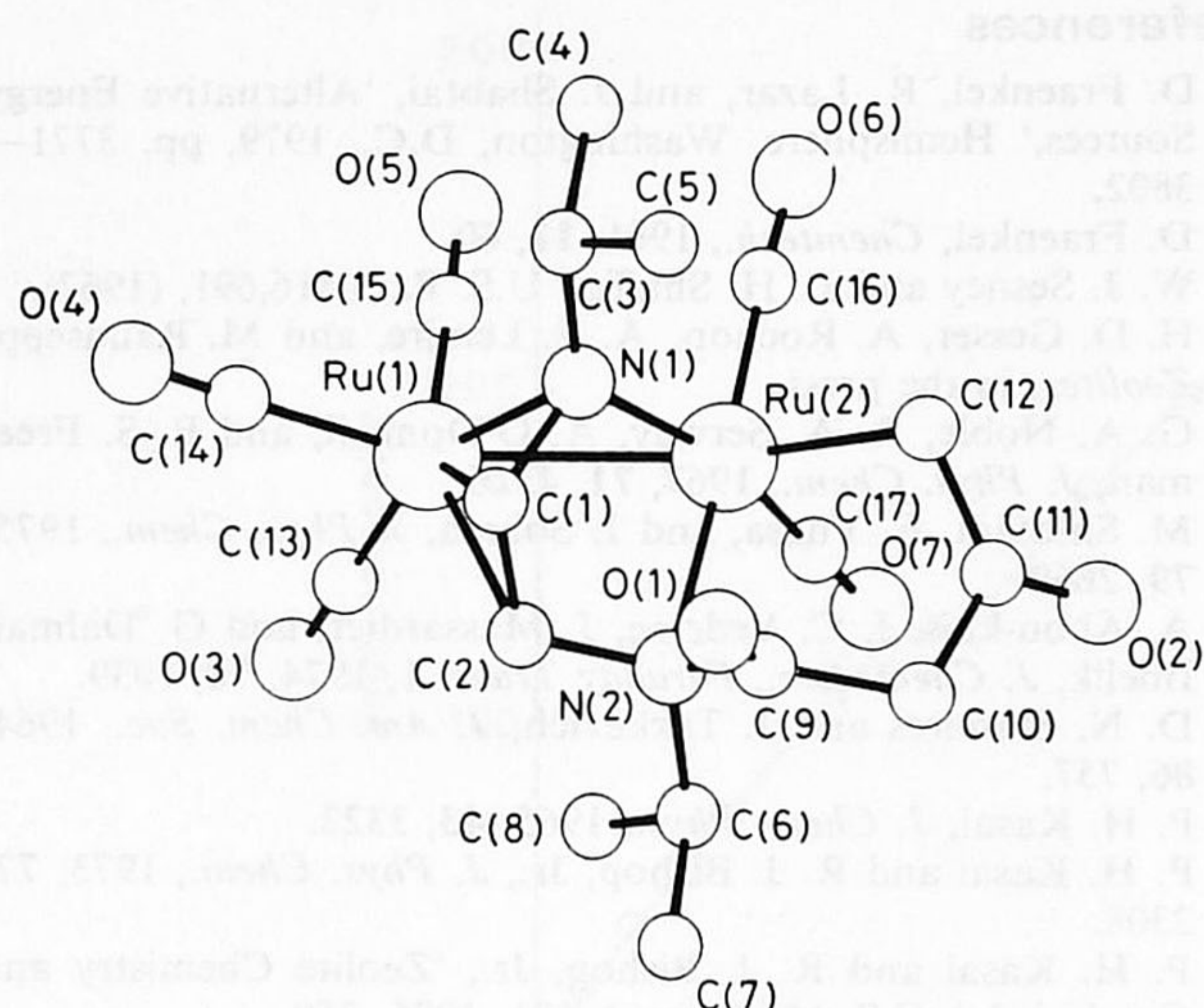
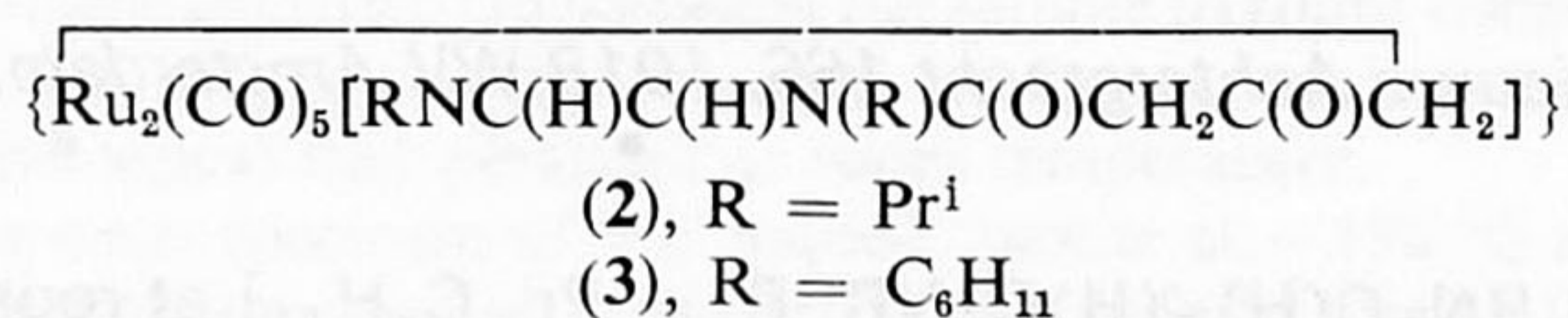
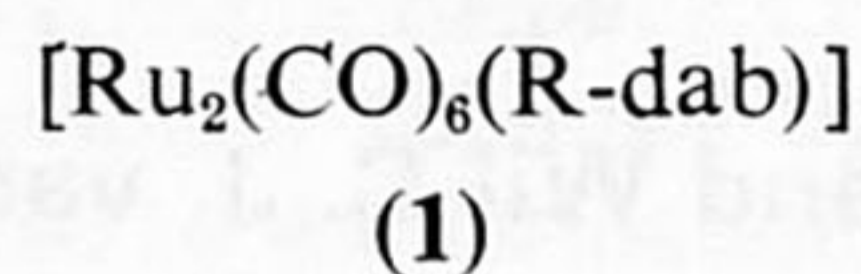


Figure 1. Molecular structure of $\{Ru_2(CO)_5[Pr^1NC(H)C(H)N-Pr^1]C(O)CH_2C(O)CH_2\}$ (2). Important bond lengths are: Ru(1)–Ru(2), 2.752(1); Ru(1)–N(1), 2.178(5); Ru(1)–C(1), 2.159(6); Ru(1)–C(2), 2.285(6); Ru(2)–N(1), 2.154(4); Ru(2)–N(2), 2.215(4); Ru(2)–C(12), 2.200(6); C(11)–C(12), 1.438(9); C(10)–C(11), 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 $[Ru_2(CO)_6(R-dab)]$ (1) (R = Pr¹, C₆H₁₁, 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 = Pr¹ (2), R = C₆H₁₁ (3)]. In the case of R = Bu^t no reaction occurred under the conditions used.



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

Crystal data for (2): C₁₇H₂₀N₂O₇Ru₂; *M* = 566.49, monoclinic, space group *P*2₁/*a*, *a* = 13.4462(8), *b* = 18.5488(2), *c* = 8.3238(4) Å, β = 103.23(1)°, *Z* = 4. A total of 3230 intensities were measured on a Nonius CAD4 diffractometer using graphite monochromated Cu–K_α radiation; 34 were below the 2.5σ(*I*) level and were treated as unobserved. An

† 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.

absorption correction was applied ($\mu = 127.7 \text{ cm}^{-1}$; 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 Δ*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 Ru₂(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 Pr¹-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 η³-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 η³-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

RuCH₂C(O)CH₂C(O)N(Pr¹)-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 CH₂Cl₂ 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 ¹³C n.m.r. spectra in CDCl₃ 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 δ_H 7.36 and 3.64 respectively with a coupling constant of 2.2 Hz.§ The C(1) and C(2) signals appear at δ_C 104.4 and 57.1 p.p.m. respectively. These values may be compared with

those of $\{MnFe(CO)_6[Pr^1NC(H)C(H)N(H)Pr^1]\}$ ¹² which appear for the H atoms at δ 6.69 and 3.40 respectively (*J* 2 Hz) and for the corresponding carbon atoms at δ_C 101.1 and 58.0 p.p.m. respectively. The CO groups absorb around δ_C 200.6 p.p.m., while the ketonic CO and the –N–CO–CH₂– appear at δ_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 $[Ru_2(CO)_6(R-dab)]$ 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.¹⁶ Secondly, the coupling of the open diketene unit to one of the N atoms of the di-imine moiety instead of the hitherto

‡ These distances may be compared with the similar bond lengths of 1.38(2) and 1.39(2) Å in $\{MnFe(CO)_6[Pr^1NC(H)C(H)N(H)Pr^1]\}$ 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 η^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 $[\text{Ru}_2(\text{CO})_6(\text{R-dab})]$ does not produce such complexes. It is interesting to note that $[\text{Ru}_2(\text{CO})_6(\text{Bu}^t\text{-dab})]$ 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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Synthesis and Crystal Structure of $[\text{PPh}_4]_2[\text{MoS}_4(\text{CuBr})_4] \cdot \text{Me}_2\text{CO}$; the Assembly of Four Copper(I) Centres about a Tetrathiomolybdate(VI) Moiety

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Reaction of $[\text{MoS}_4]^{2-}$ with CuX (1:4) in acetone produces the mixed-metal-sulphur complex anions $[\text{MoS}_4(\text{CuX})_4]^{2-}$ ($\text{X} = \text{Cl}$ or Br); a crystal structure determination for $[\text{PPh}_4]_2[\text{MoS}_4(\text{CuBr})_4] \cdot \text{Me}_2\text{CO}$ shows that four edges of the tetrahedral MoS_4 core are bridged by Cu^{I} atoms, giving an aggregate of approximate D_{2d} symmetry, with μ_2 -Br bridges linking these aggregates to form a one-dimensional polymeric anion.

The characterisation of discrete Cu–Mo–S aggregates is currently undergoing significant developments.^{1–6} The intrinsic chemical interest in these systems is stimulated by the need to improve the chemical basis for the interpretation of Cu–Mo–S interactions in biological systems, especially the molybdenum-induced copper deficiency in ruminant animals.^{7,8}

Herein, we report that $[\text{PPh}_4]_2[\text{MoS}_4]$ reacts with CuX ($\text{X} = \text{Cl}$ or Br) (1:4) in acetone, to afford the corresponding $[\text{PPh}_4]_2[\text{MoS}_4(\text{CuX})_4]$ salt as the major reaction product. Crystals of $[\text{PPh}_4]_2[\text{MoS}_4(\text{CuBr})_4] \cdot \text{Me}_2\text{CO}$ from the preparation were suitable for X-ray crystallographic study.

Crystal data: $\text{C}_{51}\text{H}_{46}\text{Br}_4\text{Cu}_4\text{MoOP}_2\text{S}_4$, $M_r = 1534.85$, triclinic, $P\bar{1}$, $a = 12.478(2)$, $b = 16.783(2)$, $c = 27.461(3)$ Å, $\alpha = 79.35(1)$, $\beta = 88.84(1)$, $\gamma = 82.00(1)^\circ$, $U = 5596.7$ Å³, $Z = 4$, $D_c = 1.82$, $D_m = 1.8$ g cm⁻³, $F(000) = 3008$, Mo- K_α radiation, $\lambda = 0.71069$ Å, $\mu = 47.79$ cm⁻¹. Data were collected to $2\theta_{\text{max}} = 45^\circ$ on a Stoe-Siemens diffractometer; of 14546 reflections, 8352 with $F > 4\sigma(F)$ were used for structure determination by Patterson and Fourier methods. Least-squares refinement with anisotropic thermal parameters for heavy atoms, isotropic for C and O, no H atoms, and phenyl rings constrained as ideal hexagons of side 1.395 Å, gave a

final R of 0.079; $R_w = [\sum_w(F_o - F_c)^2 / \sum_w F_o^2]^{1/2} = 0.065$, with $w^{-1} = \sigma^2(F) + 0.00009(F)^2$. Data were corrected for absorption by a semi-empirical method.†

The structure contains, as crystallographically independent units, four $[\text{PPh}_4]^+$ cations, two acetone molecules, and two $[\text{MoS}_4(\text{CuBr})_4]^{2-}$ anions. Each molybdenum atom of the structure (Figure 1) is at the centre of an essentially tetrahedral MoS_4 unit, in which the mean Mo–S bond length is 2.235(6) Å [maximum 2.242(6), minimum 2.227(5) Å], and the S–Mo–S angles lie between 108.3(1) and 111.1(1)°. Four copper atoms are bound to the MoS_4 core: each is symmetrically attached to one edge of the tetrahedron. The overall arrangement involves each sulphur atom bonding to two copper atoms with Cu–S bond lengths ranging from 2.237(5) to 2.305(5) Å, so that the MoS_4Cu_4 aggregate approximates to D_{2d} symmetry. The 4:1 copper to molybdenum stoichiometry is the

† The 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.