Journal of Organometallic Chemistry, *450* (1993) 219–228

JOM 23273

Formation of the unusual alkynyl carboxamide complex, $C_2H_5N(H)C(O)C{\equiv}C[Co_2(CO)_6]CCo_3(CO)_9$

Gillian H. Worth, Brian H. Robinson and Jim Simpson

Chemistry Department, University of Otago, PO Box 56, Dunedin (New Zealand)

(Received September 24, 1992)

Abstract

The reaction of the cluster complex $HC{\equiv}C[Co_2(CO)_6]CCo_3(CO)_9$ with (or without) $BrCCo_3(CO)_9$ under Cadiot–Chodkiewicz coupling conditions gave the unusual alkynyl carboxamide complex $C_2H_5N(H)C(O)C{\equiv}C[Co_2(CO)_6]CCo_3(CO)_9$ rather than a coupled product containing two tricobalt cluster units. Steric demands imposed by the Co_3 cluster allow attack at the least hindered alkyne carbon and stabilise the formed ynamine, so allowing subsequent CO insertion. The product has been characterised by X-ray crystallography.

1. Introduction

Tricobaltcarbon clusters with alkyne functionality, such as $Me_3SiC{\equiv}CCCo_3(CO)_9$ (1), have been successfully prepared by coupling reactions between alkynes and $BrCCo_3(CO)_9$ [1]. Attempts to link two or more cluster moieties *via* alkyne chains have proved less successful, with coupling reactions involving acetylene or diacetylene giving poor yields of the required coupled products, 2 and 3. Previous reports [2,3] have demonstrated the possibility of protecting the alkyne unit by the formation of hexacarbonyldicobalt derivatives [4]. In particular, such complex formation has been utilised to protect the alkyne functionality under Friedel–Crafts conditions [3] and during carbocation formation in stereospecific ring closure reactions [5]. We were intrigued to see if similar protection was afforded to the alkyne function under conditions required for Cadiot–Chodkiewicz coupling of alkyne moieties. A preliminary investigation of the copper-catalysed coupling reaction between $HC{\equiv}C[Co_2(CO)_6]CCo_3(CO)_9$ (4) [6] and $BrCCo_3(CO)_9$ showed no evidence for the formation of the required $(CO)_9Co_3C(C{\equiv}C)[Co_2(CO)_6]CCo_3(CO)_9$ (5) [1]. Instead, reasonable yields of an amide complex, $C_2H_5N(H)C(O)C{\equiv}C[Co_2(CO)_6]CCo_3(CO)_9$ (6) were obtained. This paper reports the details of this unusual reaction and X-ray structural confirmation of the unique product.

$Me_3Si{-}C{\equiv}C{-}CCo_3(CO)_9$

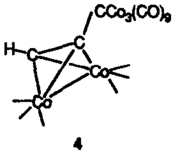
1

$(CO)_9Co_3{-}C{\equiv}C{-}CCo_3(CO)_9$

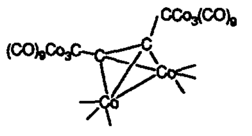
2

$(CO)_9Co_3C{-}C{\equiv}C{-}C{\equiv}C{-}CCo_3(CO)_9$

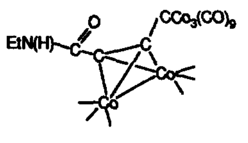
3



4



5



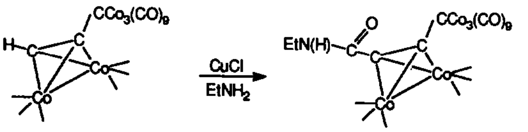
6

Correspondence to: Professor J. Simpson.

0022-328X/93/$6.00

2. Results and discussion

Attempts to couple $HC{\equiv}C[Co_2(CO)_6]CCo_3(CO)_9$ (**4**) and $BrCCo_3(CO)_9$ under Cadiot–Chodkiewicz conditions were singularly unsuccessful. The reaction of $HC{\equiv}C[Co_2(CO)_6]CCo_3(CO)_9$ with $EtNH_2$ in the presence of CuCl led inevitably to the facile formation of the novel alkynyl carboxamide complex $C_2H_5N(H)C(O)C{\equiv}C[Co_2(CO)_6]CCo_3(CO)_9$ (**6**) (eqn. (1)). It was found that both the reaction product and approximate yield of **6** were independent of the presence of the bromo cluster, $BrCCo_3(CO)_9$ but, if the reaction is carried out in an atmosphere of CO, the yield is increased significantly.



(1)

The mass spectrum of **6** showed a weak parent ion and sequential loss of 16 carbonyl groups; loss of one additional carbonyl group to the number of metal bound groups is characteristic of $Co_3(CO)_9C(CO)X$ functionality [7] and offers good evidence for the carboxamide formulation. The infrared spectrum of the molecule in the carbonyl region is a complex aggregate of the idealised five-band spectrum of the tricobaltcarbon unit [8] and up to six bands from the dicobalthexacarbonyl fragment [4]. Nine bands are readily resolved in the region 2108–2014 cm^{-1} and the two highest energy bands at 2108 and 2085 cm^{-1} can be assigned to the totally symmetric vibrations of the carbonyl groups of the tricobalt and dicobalt moieties respectively. In addition the carboxamide $\nu(CO)$ is observed at 1730 cm^{-1}.

To our knowledge this is the first $Co_2(CO)_6$ complex of an alkynyl carboxamide and confirmation of the detailed structure of **6** was sought from an X-ray crystal structure analysis. There are two independent molecules in the asymmetric unit of the monoclinic unit cell of **6**. Perspective views of these molecules are shown in Fig. 1 which also shows the atom numbering scheme, with selected bond length and angle information in Table 1. The structure consists of discrete molecules, with the closest intermolecular contact (not involving H atoms) being 2.83(2) Å between O(131) atoms. The discrete molecular units exhibit minor variations in bond lengths and angles and also differ significantly in the relative orientations of the $Co_2(CO)_6$ units and their amide substituents with respect to the planes of the Co_3 triangles. Unless otherwise stated, molecular parameters for molecule **1** will be used in the subsequent discussion.

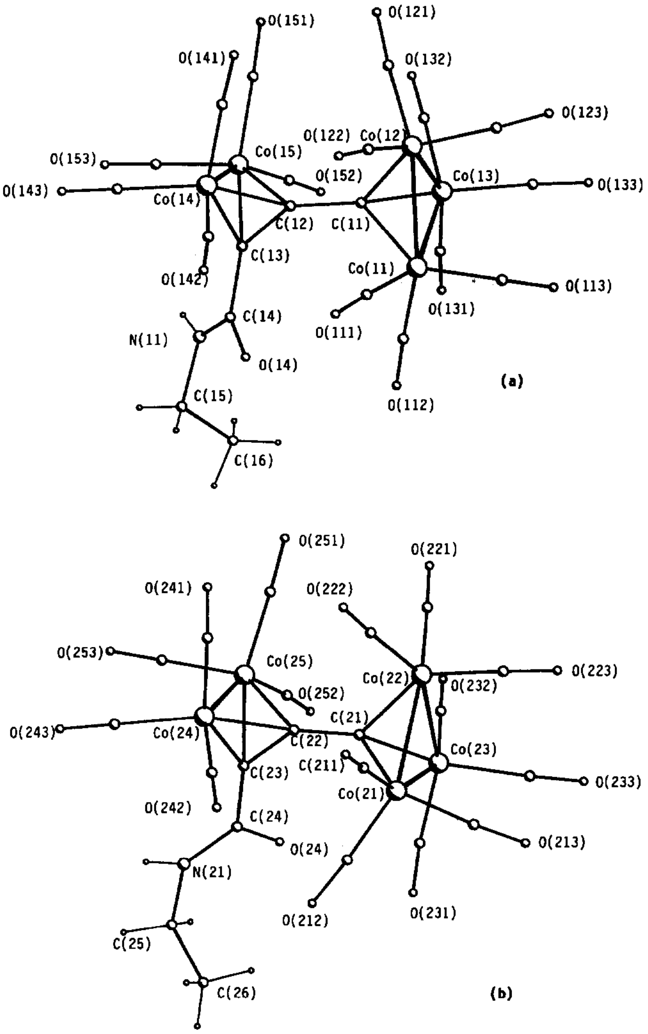


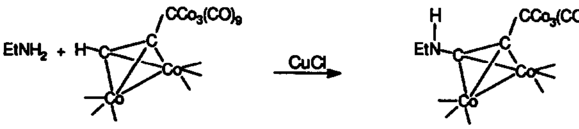
Fig. 1. Perspective views of the two unique molecules of $C_2H_5N(H)C(O)C{\equiv}C[Co_2(CO)_6]CCo_3(CO)_9$ (**6**) showing the atom numbering schemes. (a) molecule 1; (b) molecule 2.

The structure is that of a (μ-alkyne)hexacarbonyldicobalt complex with an ethylamide as one alkyne substituent and a methylidynetricobalt nonacarbonyl moiety as the other. The hexacarbonyldicobalt fragment has the alkyne C≡C bond approximately perpendicular to the Co–Co bond [interline angle 88.7(8)°] [9] and there is a classical 'sawhorse' arrangement of the carbonyl ligands with respect to the two cobalt atoms [10]. The C(12)≡C(13) (1.34(2) Å) and Co(14)-Co(15) (2.461(2) Å) distances are normal [11], and the bend back angles 42° and 37° subtended by the alkyne substituents at C(12) and C(13) respectively [12] indicate relatively little steric interaction between the alkyne dicobalt moiety and its amide and cluster substituents. The Co_3C unit of the cluster substituent on the alkyne is found to be a reasonably symmetric pyramid as is characteristic of this grouping with normal Co–Co [mean 2.46(1) Å] and Co–C [mean 1.93(1) Å] distances

[13]. Each cobalt atom carries the expected two equatorial and one axial carbonyl ligands, and close contacts between the equatorial carbonyl groups of the cluster and those of the dicobalt acetylene moiety result in a characteristic reduction in the dihedral angles between the Co_3 meanplane and the meanplanes containing the Co and associated carbonyl groups. The C(11)–C(12) bond linking the tricobalt and dicobalt moieties is 1.47(2) Å long, closely similar to that found in the related molecule $HC{\equiv}C[Co_2(CO)_6]$-$CCo_3(CO)_9$ (4) [6]. However, in contrast to the parent molecule, this bond is almost orthogonal to the plane of the Co_3 triangle with the angles C(12)–C(11)–Co equal within experimental error, and the angle between the C(1)–C(2) bond vector and the perpendicular to the Co_3 meanplane is 2.1(5)°.

The second substituent on the bridging alkyne is a simple ethylamide group linked to the alkyne carbon atom by the C(13)–C(14) bond of length 1.46(2) Å. Other bond distances and angles within the amide fragment are unremarkable and, as expected, the atoms C(13) C(14) O(14) N(11) and C(15) of the amide function are coplanar.

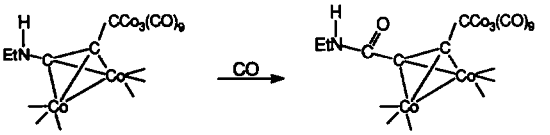
Alkynyl carboamides are normally produced from halo precursors [14], and the Cu(I) catalysed reaction of a terminal acetylene complex and an amine to give a carboxamide has not been reported previously. Primary amines normally react with terminal acetylenes under Cadiot-Chodkiewicz coupling conditions to give Schiff base compounds and addition products but Schiff base formation is not possible with **4** as a substrate. Since the catalysed reaction (eqn. (1)) does *not* take place with a $Co_2(CO)_6$ derivative of a terminal acetylene (*e.g.* $PhC{\equiv}C[Co_2CO)_6]H$), it is the tricobaltcarbon cluster which is providing the electronic and steric features required for the reaction to occur. A clue to the mechanism of the reaction is the report [15] that copper-catalysed oxidation of Ph–C≡C–H with secondary amines under Glaser coupling conditions leads to ynamines; there was indirect evidence that ynamines were intermediates in reactions with primary amines. It is therefore reasonable to suggest that the initial product in reaction (1) is a cluster ynamine arising from direct attack of the amine on the coordinated acetylene (eqn. (2) at the more open end of the carbyne chain.



(2)

Activation of the coordinated alkyne would be facilitated by the electron-withdrawing capability of the Co_3C unit [13,16] and, because the triple bond is coordinated to the $Co_2(CO)_6$ fragment, allenisation is avoided. Stabilisation of the ynamine results from the steric protection afforded by the equatorial carbonyl 'umbrella' of the CCo_3 cluster substituent on the alkyne which blocks further reaction. Hydration of the C≡C bond of an ynamine is a known route to amides [15], but this pathway is blocked by the incorporation of the alkyne unit into the alkyne dicobalt complex. Furthermore, our results show that formation of the alkynyl carboxamide requires the presence of the CCo_3 cluster as an alkyne substituent indicating that the amide carbonyl is derived from an intramolecular reaction. Mechanistically it is difficult to visualise the amine acting as a nucleophile or the Cu^I coordinating to the complexed alkyne. Formally, the ynamine can be regarded as a product from the cross-coupling of an aminium radical and a cluster radical, stabilised by the steric protection afforded by the cluster unit.

Ynamines while thermally stable are usually very reactive [14] and the subsequent intramolecular insertion of CO to give a carboxamide (eqn. (3)) is clearly possible given the close proximity of the Co–CO groups.

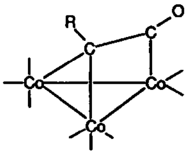


(3)

Where insertion occurs with terminal alkyne–$Co_2(CO)_6$ complexes it generally results in breakdown of the complex species (eqn. (4)) followed by a series of additional steps leading to the formation of a variety of products ranging from esters to cyclopentadienones [4,17].

$$(H_2C_2H)Co_2(CO)_6 \xrightarrow{CO,EtOH} CH_2=CHCO_2Et \qquad (4)$$

Carbonyl-insertion reactions of the more robust tricobaltcarbon cluster to give acyl derivatives are well known and migration of ligated CO to the apical carbyne atom of the cluster is accelerated by the presence of amines and other nucleophiles [18]. The intimate mechanism of carbon monoxide insertion reactions with these clusters is not well understood [19]. Migratory insertion of a CO ligand into a C–Co bond through an intermediate such as 7 has been suggested [20] and support for this proposal can be found in the observation that intramolecular decarbonylation of acyl cluster complexes occurs *via* migration of the acyl CO group to an equatorial site on the cobalt triangle [21]. This



7

TABLE 1. Bond lengths and angles for $C_2H_5N(H)C(O)C{\equiv}C[Co_2(CO_6]CCo_3(CO)_9$ (**6**)

Molecule 1		Molecule 2	
Bond lengths			
Co(11)–Co(12)	2.478(3)	Co(21)–Co(22)	2.460(3)
Co(11)–Co(13)	2.456(2)	Co(21)–Co(23)	2.455(2)
Co(11)–C(11)	1.921(1)	Co(21)–C(21)	1.93(1)
Co(11)–C(111)	1.79(2)	Co(21)–C(211)	1.80(2)
Co(11)–C(112)	1.78(2)	Co(21)–C(212)	1.76(2)
Co(11)–C(113)	1.85(2)	Co(21)–C(213)	1.81(2)
Co(12)–Co(13)	2.446(3)	Co(22)–Co(23)	2.459(3)
Co(12)–C(11)	1.92(1)	Co(22)–C(21)	1.91(1)
Co(12)–C(121)	1.78(1)	Co(22)–C(221)	1.80(2)
Co(12)–C(121)	1.78(1)	Co(22)–C(221)	1.80(2)
Co(12)–C(122)	1.79(2)	Co(22)–C(222)	1.84(2)
Co(12)–C(123)	1.81(2)	Co(22)–C(223)	1.81(2)
Co(13)–C(11)	1.94(1)	Co(23)–C(21)	1.91(1)
Co(13)–C(131)	1.78(2)	Co(23)–C(231)	1.82(2)
Co(13)–C(132)	1.83(2)	Co(23)–C(232)	1.84(1)
Co(13)–C(133)	1.83(2)	Co(23)–C(233)	1.86(2)
Co(14)–Co(15)	2.461(2)	Co(24)–Co(25)	2.472(3)
Co(14)–C(12)	1.95(1)	Co(24)–C(22)	2.01(1)
Co(14)–C(13)	1.96(1)	Co(24)–C(23)	1.96(1)
Co(14)–C(141)	1.81(2)	Co(24)–C(241)	1.83(2)
Co(14)–C(142)	1.79(2)	Co(24)–C(242)	1.79(2)
Co(14)–C(143)	1.83(2)	Co(24)–C(243)	1.83(2)
Co(15)–C(12)	1.97(1)	Co(25)–C(22)	1.97(1)
Co(15)–C(13)	1.94(1)	Co(25)–C(23)	1.96(1)
Co(15)–C(151)	1.81(1)	Co(25)–C(251)	1.80(2)
Co(15)–C(152)	1.80(1)	Co(25)–C(252)	1.83(2)
Co(15)–C(153)	1.83(1)	Co(25)–C(253)	1.83(2)
C(11)–C(12)	1.47(2)	C(21)–C(22)	1.44(2)
C(12)–C(13)	1.34(2)	C(22)–C(23)	1.37(2)
C(13)–C(14)	1.46(2)	C(23)–C(24)	1.47(2)
C(14)–O(14)	1.24(2)	C(24)–O(24)	1.24(2)
C(14)–N(11)	1.32(2)	C(24)–N(21)	1.33(2)
N(11)–C(15)	1.47(2)	N(21)–C(25)	1.44(2)
C(15)–C(16)	1.48(2)	C(25)–C(26)	1.49(2)
C(111)–O(111)	1.13(2)	C(211)–O(211)	1.12(2)
C(112)–O(112)	1.16(2)	C(212)–O(212)	1.16(2)
C(113)–O(113)	1.14(2)	C(213)–O(213)	1.14(2)
C(121)–O(121)	1.15(2)	C(221)–O(221)	1.12(2)
C(122)–O(122)	1.15(2)	C(222)–O(222)	1.11(2)
C(123)–O(123)	1.14(2)	C(223)–O(223)	1.17(2)
C(131)–O(131)	1.14(2)	C(231)–O(231)	1.10(2)
C(132)–O(132)	1.11(2)	C(232)–O(232)	1.11(2)
C(133)–O(133)	1.13(2)	C(233)–O(233)	1.11(2)
C(141)–O(141)	1.14(2)	C(241)–O(241)	1.14(2)
C(142)–O(142)	1.15(2)	C(242)–O(242)	1.14(2)
C(143)–O(143)	1.13(2)	C(243)–O(243)	1.13(2)
C(151)–O(151)	1.12(2)	C(251)–O(251)	1.16(2)
C(152)–O(152)	1.14(2)	C(252)–O(252)	1.10(2)
C(153)–O(153)	1.13(2)	C(253)–O(253)	1.14(2)
Bond angles			
Co(12)–Co(11)–Co(13)	59.4(1)	Co(22)–Co(21)–Co(23)	60.0(1)
Co(12)–Co(11)–C(11)	49.9(4)	Co(22)–Co(21)–C(21)	49.7(4)
Co(12)–Co(11)–C(111)	99.8(5)	Co(22)–Co(21)–C(211)	92.0(5)
Co(12)–Co(11)–C(112)	150.6(5)	Co(22)–Co(21)–C(212)	145.3(5)
Co(12)–Co(11)–C(113)	97.5(5)	Co(22)–Co(21)–C(213)	105.2(5)
Co(13)–Co(11)–C(11)	50.7(4)	Co(23)–Co(21)–C(21)	50.0(4)
Co(13)–Co(11)–C(111)	151.5(5)	Co(23)–Co(21)–C(211)	151.7(5)
Co(13)–Co(11)–C(112)	96.6(5)	Co(23)–Co(21)–C(212)	100.6(5)
Co(13)–Co(11)–C(113)	100.6(5)	Co(23)–Co(21)–C(213)	93.4(5)

TABLE 1 (continued)

Molecule 1		Molecule 2	
Bond angles			
C(11)-Co(11)-C(111)	101.4(6)	C(21)-Co(21)-C(211)	109.6(6)
C(11)-Co(11)-C(112)	102.5(6)	C(21)-Co(21)-C(212)	95.6(6)
C(11)-Co(11)-C(113)	142.9(6)	C(21)-Co(21)-C(213)	141.4(6)
C(111)-Co(11)-C(112)	95.3(7)	C(211)-Co(21)-C(212)	101.0(7)
C(111)-Co(11)-C(113)	101.5(7)	C(211)-Co(21)-C(213)	98.7(7)
C(112)-Co(11)-C(113)	104.0(7)	C(212)-Co(21)-C(213)	104.5(7)
Co(11)-Co(12)-Co(13)	59.8(1)	Co(21)-Co(22)-Co(23)	59.9(1)
Co(11)-Co(12)-C(11)	49.9(4)	Co(21)-Co(22)-C(21)	50.4(4)
Co(11)-Co(12)-C(121)	152.6(4)	Co(21)-Co(22)-C(221)	152.2(5)
Co(11)-Co(12)-C(122)	96.0(5)	Co(21)-Co(22)-C(222)	100.0(6)
Co(11)-Co(12)-C(123)	101.3(5)	Co(21)-Co(22)-C(223)	97.0(5)
Co(13)-Co(12)-C(11)	50.9(4)	Co(23)-Co(22)-C(21)	50.1(4)
Co(13)-Co(12)-C(121)	99.6(4)	Co(23)-Co(22)-C(221)	95.8(5)
Co(13)-Co(12)-C(122)	152.2(5)	Co(23)-Co(22)-C(222)	151.9(6)
Co(13)-Co(12)-C(123)	96.9(5)	Co(23)-Co(22)-C(223)	99.1(5)
C(11)-Co(12)-C(121)	103.7(6)	C(21)-Co(22)-C(221)	104.5(6)
C(11)-Co(12)-C(122)	103.9(6)	C(21)-Co(22)-C(222)	102.4(7)
C(11)-Co(12)-C(123)	143.1(6)	C(21)-Co(22)-C(223)	141.7(6)
C(121)-Co(12)-C(122)	98.0(7)	C(221)-Co(22)-C(222)	97.1(8)
C(121)-Co(12)-C(123)	98.9(7)	C(221)-Co(22)-C(223)	100.2(7)
C(122)-Co(12)-C(123)	101.5(7)	C(222)-Co(22)-C(223)	103.0(8)
Co(11)-Co(13)-Co(12)	60.7(1)	Co(21)-Co(23)-Co(22)	60.1(1)
Co(11)-Co(13)-C(11)	50.2(4)	Co(21)-Co(23)-C(21)	50.5(4)
Co(11)-Co(13)-C(131)	97.0(5)	Co(21)-Co(23)-C(231)	94.8(5)
Co(11)-Co(13)-C(132)	151.7(5)	Co(21)-Co(23)-C(232)	151.9(5)
Co(11)-Co(13)-C(133)	99.5(4)	Co(21)-Co(23)-C(233)	101.8(4)
Co(12)-Co(13)-C(11)	50.4(4)	Co(22)-Co(23)-C(21)	49.8(4)
Co(12)-Co(13)-C(131)	154.8(5)	Co(22)-Co(23)-C(231)	152.0(5)
Co(12)-Co(13)-C(132)	97.6(5)	Co(22)-Co(23)-C(232)	98.1(5)
Co(12)-Co(13)-C(133)	96.8(5)	Co(22)-Co(23)-C(233)	99.8(5)
C(11)-Co(13)-C(131)	107.0(6)	C(21)-Co(23)-C(231)	105.7(6)
C(11)-Co(13)-C(132)	102.4(6)	C(21)-Co(23)-C(232)	102.4(6)
C(11)-Co(13)-C(133)	141.6(6)	C(21)-Co(23)-C(233)	144.6(6)
C(131)-Co(13)-C(132)	98.7(7)	C(231)-Co(23)-C(232)	100.9(6)
C(131)-Co(13)-C(133)	98.8(7)	C(231)-Co(23)-C(233)	97.3(7)
C(132)-Co(13)-C(133)	101.1(6)	C(232)—Co(23)-C(233)	99.2(6)
Co(15)-Co(14)-C(12)	51.4(3)	Co(25)-Co(24)-C(22)	50.9(4)
Co(15)-Co(14)-C(13)	50.4(4)	Co(25)-Co(24)-C(23)	50.9(4)
Co(15)-Co(14)-C(141)	101.0(4)	Co(25)-Co(24)-C(241)	97.1(4)
Co(15)-Co(14)-C(142)	150.5(5)	Co(25)-Co(24)-C(242)	150.1(5)
Co(15)-Co(14)-C(143)	96.9(4)	Co(25)-Co(24)-C(243)	101.0(5)
C(12)-Co(14)-C(13)	40.3(5)	C(22)-Co(24)-C(23)	40.3(6)
C(12)-Co(14)-C(141)	103.9(6)	C(22)-Co(24)-C(241)	107.8(6)
C(12)-Co(14)-C(142)	103.8(6)	C(22)-Co(24)-C(242)	100.2(6)
C(12)-Co(14)-C(143)	140.6(6)	C(22)-Co(24)-C(243)	141.4(6)
C(13)-Co(14)-C(141)	142.0(6)	C(23)-Co(24)-C(241)	143.2(6)
C(13)-Co(14)-C(142)	100.8(6)	C(23)-Co(24)-C(242)	103.3(6)
C(13)-Co(14)-C(143)	103.2(6)	C(23)-Co(24)-C(243)	102.8(6)
C(141)-Co(14)-C(142)	100.9(6)	C(241)-Co(24)-C(242)	100.0(7)
C(141)-Co(14)-C(143)	104.9(7)	C(241)-Co(24)-C(243)	100.8(7)
C(142)-Co(14)-C(143)	96.4(6)	C(242)-Co(24)-C(243)	99.8(7)
Co(14)-Co(15)-C(12)	50.6(3)	Co(24)-Co(25)-C(22)	52.4(3)
Co(14)-Co(15)-C(13)	51.1(4)	Co(24)-Co(25)-C(23)	50.8(4)
Co(14)-Co(15)-C(151)	98.2(4)	Co(24)-Co(25)-C(251)	101.6(5)
Co(14)-Co(15)-C(152)	151.7(5)	Co(24)-Co(25)-C(252)	146.1(5)
Co(14)-Co(15)-C(153)	100.1(4)	Co(24)-Co(25)-C(253)	96.3(4)
C(12)-Co(15)-C(13)	40.3(5)	C(22)-Co(25)-C(23)	40.7(6)
C(12)-Co(15)-C(151)	106.7(6)	C(22)-Co(25)-C(251)	103.3(7)
C(12)-Co(15)-C(152)	102.4(6)	C(22)-Co(25)-C(252)	101.7(6)
C(12)-Co(15)-C(153)	142.5(6)	C(22)-Co(25)-C(253)	143.4(6)
C(13)-Co(15)-C(151)	143.4(6)	C(23)-Co(25)-C(251)	142.0(6)
C(13)-Co(15)-C(152)	104.1(6)	C(23)-Co(25)-C(252)	95.5(6)

TABLE 1 (continued)

C(13)–Co(15)–C(153)	104.8(6)	C(23)–Co(25)–C(253)	106.7(6)
C(151)–Co(15)–C(152)	98.1(6)	C(251)–Co(25)–C(252)	106.1(7)
C(151)–Co(15)–C(153)	99.6(6)	C(251)–Co(25)–C(253)	101.4(7)
C(152)–Co(15)–C(153)	99.7(6)	C(252)–Co(25)–C(253)	96.9(7)
Co(11)–C(11)–Co(12)	80.3(5)	Co(21)–C(21)–Co(22)	79.9(5)
Co(11)–C(11)–Co(13)	79.1(5)	Co(21)–C(21)–Co(23)	79.5(5)
Co(11)–C(11)–C(12)	130.5(9)	Co(21)–C(21)–C(22)	130.6(9)
Co(12)–C(11)–Co(13)	78.7(5)	Co(22)–C(21)–Co(23)	80.2(5)
Co(12)–C(11)–C(12)	133.6(9)	Co(22)–C(21)–C(22)	135(1)
Co(13)–C(11)–C(12)	133.4(9)	Co(23)–C(21)–C(22)	130.4(9)
Co(14)–C(12)–Co(15)	78.0(5)	Co(24)–C(22)–Co(25)	76.7(5)
Co(14)–C(12)–C(11)	135.1(9)	Co(24)–C(22)–C(21)	133.2(9)
Co(14)–C(12)–C(13)	70.3(8)	Co(24)–C(22)–C(23)	67.6(7)
Co(15)–C(12)–C(11)	132.5(9)	Co(25)–C(22)–C(21)	137.3(9)
Co(15)–C(12)–C(13)	68.7(7)	Co(25)–C(22)–C(23)	69.2(8)
C(11)–C(12)–C(13)	143(1)	C(21)–C(22)–C(23)	143(1)
Co(14)–C(13)–Co(15)	78.5(5)	Co(24)–C(23)–Co(25)	78.3(5)
Co(14)–C(13)–C(12)	69.4(8)	Co(24)–C(23)–C(22)	72.1(8)
Co(14)–C(13)–C(14)	128.8(9)	Co(24)–C(23)–C(24)	142(1)
Co(15)–C(13)–C(12)	71.1(7)	Co(25)–C(23)–C(22)	70.1(8)
Co(15)–C(13)–C(14)	141.9(9)	Co(25)–C(23)–C(24)	127.3(9)
C(12)–C(13)–C(14)	138(1)	C(22)–C(23)–C(24)	137(1)
C(13)–C(14)–O(14)	121(1)	C(23)–C(24)–O(24)	120(1)
C(13)–C(14)–N(11)	116(1)	C(23)–C(24)–N(21)	115(1)
O(14)–C(14)–N(11)	122(1)	O(24)–C(24)–N(21)	123(1)
C(14)–N(11)–C(15)	123(1)	C(24)–N(21)–C(25)	121(1)
N(11)–C(15)–C(16)	112(1)	N(21)–C(25)–C(26)	112(1)
Co(11)–C(111)–O(111)	176(1)	Co(21)–C(211)–O(211)	177(2)
Co(11)–C(112)–O(112)	177(1)	Co(21)–C(212)–O(212)	176(1)
Co(11)–C(113)–O(113)	178(1)	Co(21)–C(213)–O(213)	176(1)
Co(12)–C(121)–O(121)	175(1)	Co(22)–C(221)–O(221)	178(1)
Co(12)–C(122)–O(122)	175(1)	Co(22)–C(222)–O(222)	175(2)
Co(12)–C(123)–O(123)	175(1)	Co(22)–C(223)–O(223)	178(1)
Co(13)–C(131)–O(131)	177(1)	Co(23)–C(231)–O(231)	174(1)
Co(13)–C(132)–O(132)	177(1)	Co(23)–C(232)–O(232)	178(1)
Co(13)–C(133)–O(133)	177(1)	Co(23)–C(233)–O(233)	177(1)
Co(14)–C(141)–O(141)	177(1)	Co(24)–C(241)–O(241)	176(1)
Co(14)–C(142)–O(142)	174(1)	Co(24)–C(242)–O(242)	179.6(8)
Co(14)–C(143)–O(143)	179(1)	Co(24)–C(243)–O(243)	179(1)
Co(15)–C(151)–O(151)	178(1)	Co(25)–C(251)–O(251)	177(1)
Co(15)–C(152)–O(152)	178(1)	Co(25)–C(252)–O(252)	175(1)
Co(15)–C(153)–O(153)	178(1)	Co(25)–C(253)–O(253)	179.7(6)

route should also be open to the $Co_2(CO)_6$ systems, and the classic formation of acrylate, propionate and succinate esters from the reaction of the archetypal $HC{\equiv}CH[Co_2(CO)_6]$ with CO in ethanol [22] can be explained in terms of CO insertion into the Co–$C_{acetylene}$ bonds followed by breakup of the bridged dicobalt complex with the extrusion of $Co_2(CO)_8$ or $HCo(CO)_4$. However the presence of the bulky $CCo_3(CO)_9$ substituent evidently stabilises the carboxamide–$Co_2(CO)_6$ products by blocking loss of the $Co_2(CO)_6$ moiety.

The unusual reaction reported here is another example of the way in which the electronic and steric demands of the tricobaltcarbon cluster [13,23] can be used to influence the reactivity of coordinated organic moieties. Further work is in progress in an attempt to explore the scope and utility of this novel chemistry.

3. Experimental details

All reactions were carried out under argon or nitrogen in purified, dried solvents. The compounds $HC{\equiv}C[Co_2(CO)_6]CCo_3(CO)_9$ (4) [6], $BrCCo_3(CO)_9$ [24] and CuCl [25] were prepared by published methods. Infrared spectra were recorded on a Digilab FX60 spectrometer. FAB mass spectra were recorded on a

TABLE 2. Crystal data, data collection and refinement for $C_2H_5N(H)C(O)C{\equiv}C[Co_2(CO)_6]CCo_3(CO)_9$ (**6**)

Empirical formula	$C_{21}H_6O_{16}NCo_5$
M/g mol^{-1}	822.95
Crystal system	Monoclinic
Space group	$P2_1/n$ (No. 14) [a]
a/Å	9.504(7)
b/Å	35.537(21)
c/Å	16.841(13)
α/°	90
β/°	94.45(6)
γ/°	90
V/Å^3	5511(7)
D_c/g cm^{-3}	1.98
Z	8 [b]
Crystal size/mm	0.38×0.38×0.02
μ(Mo Kα) cm^{-1}	29.47
F(000)	2615
Diffractometer:	Nicolet R3M
Temperature/K	123±5
Radiation:	Mo Kα (λ = 0.71069 Å)
Scan type:	$\theta - 2\theta$
Scan speed/deg min^{-1}	Variable, max 29.0 min 4.0
Data limits/°	$3 < 2\theta < 45$
Reflections measured	$h, k, \pm l$
Crystal decay [b]	< 7% [c]
Absorption correction	analytical [d]
Transmission	0.942 (maximum) 0.599 (minimum)
Total reflections	6814 [d]
Unique data ($I > 2\sigma I$)	4004
Method of solving	Direct methods
Number of variables	316 [e]
Treatment of protons	calculated
$R(\Sigma\Delta F/\Sigma\lvert F_o\rvert)$	0.0623
$R_w[\Sigma w^{1/2}(\Delta F)/\Sigma w^{1/2}F_o]$	0.0636
Weight (w)	$[1.4589/(\sigma^2F + 0.00089F^2)]$
Residual density e Å^{-3}	0.74–0.76

[a] A non-standard setting of $P2_1/c$ (No 14), reference 27. [b] Two unique molecules in the asymmetric unit. [c] Standard reflections (4 0 0) (0 18 0) (0 0 4) measured after every 100 reflections. [d] Lorentz and polarisation and absorption corrections were applied using the SHELXTL system, reference 28. [e] In each alternating blocked matrix cycle.

VG ZAB 2HF instrument at the University of Adelaide. Elemental analyses were performed by the Microanalytical Service, University of Otago.

3.1. Reaction of $HC{\equiv}C[Co_2(CO)_6]CCo_3(CO)_9$ with $BrCCo_3(CO)_9$

$BrCCo_3(CO)_9$ (0.25 g) in dioxane (3 cm^3) was added dropwise to a solution of dioxane (3 cm^3) containing $HC{\equiv}C[Co_2(CO)_6]CCo_3(CO)_9$ (0.30 g), $EtNH_2$ (50 mg), and CuCl (20 mg). An exothermic reaction occurred and the temperature was maintained below 29°C. The mixture was stirred for a further 30 min, then filtered and the residue washed with CH_2Cl_2. The solvent was removed under reduced pressure and the remaining solid subjected to preparative TLC on silica plates with CH_2Cl_2 eluent. Five significant bands were obtained: (1) purple $BrCCo_3(CO)_9$ (0.12 g); (2) green $HC{\equiv}C[Co_2(CO)_6]CCo_3(CO)_9$ (0.18 g); (3) orange $C_2[CCo_3(CO)_9]_2$ [26], (35 mg); (4) green (30 mg); (5) dark brown $EtN(H)CCo_3(CO)_9$ [1]. Band 4 was recrystallised from hexane and identified as $C_2H_5N(H)C(O)C{\equiv}C[Co_2(CO)_6]CCo_3(CO)_9$ (**6**); yield 30 mg (22%). Found C, 31.41, H, 0.94, N, 1.70 $C_{21}H_6O_{16}NCo_5$ requires C, 30.72, H, 0.74, N, 1 .71%. m/e 823 M^+. ν(CO) hexane: 2108w, 2085s, 2072vs, 2060vs, 2052w, 2043sh, 2033s, 2025sh, 2014w 1730s cm^{-1}.

Repetition of the reaction under an atmosphere of carbon monoxide, in the absence of $BrCCo_3(CO)_9$, gave the amide complex [band (4)] as the principal product in *ca.* 40% yield.

3.2. X-ray data collection, reduction and structure solution for $C_2H_5N(H)C(O)C{\equiv}C[Co_2(CO)_6]CCo_3(CO)_9$

A sample of **1** prepared as outlined above was recrystallised from hexane as green-black plates. Preliminary precession photography (Cu Kα) uniquely confirmed the monoclinic space group $P2_1/n$ (a non-standard setting of $P2_1/c$ (No. 14) [27]). Details of the crystals, data collection and structure refinement are summarised in Table 2. The structure was solved by direct methods using SHELXTL [28]. The resulting E-map revealed the location of 10 cobalt atoms, 5 from each of the two independent molecules in the asymmetric unit. The remaining non-hydrogen atoms were found in subsequent difference Fourier, least squares refinement cycles using SHELX-76 [29]. Hydrogen atoms on the amide C atoms were included as fixed contributions to F_c(d(C–H) 0.98 Å). Weighted refinement was performed with the carbon atoms of the carbonyl ligands refined isotropically and all other non-hydrogen atoms assigned anisotropic temperature factors. The two independent molecules were refined in alternating blocked-matrix cycles minimising $w(\lvert F_o\rvert - \lvert F_c\rvert)^2$. Refinement of this model converged with $R = 0.0623$ and $R_w = 0.0636$ for the 4004 observed reflections; 316 parameters were refined for each independent molecule. The final difference map showed maxima at 0.74 and −0.76 e Å^{-3}. Final positional and equivalent thermal parameters are listed for both molecules in Table 3. Tables of thermal parameters, H-atom parameters, observed and calculated structure factors, and full listings of bond length, angle and meanplane data can be obtained from the author (J.S.).

TABLE 3. Final positional and equivalent [a] thermal parameters for $C_2H_5N(H)C(O)C{\equiv}C[Co_2(CO)_6]CCo_3(CO)_9$ (6)

Atom	x	y	z	U_{eq}/U_{11}
Molecule 1				
Co(11)	0.1028(2)	0.0463(1)	0.8081(1)	0.021
Co(12)	0.2044(2)	0.0863(1)	0.7045(1)	0.021
Co(13)	0.3367(2)	0.0761(1)	0.8333(1)	0.020
Co(14)	0.3111(2)	−0.0248(1)	0.6223(1)	0.020
Co(15)	0.5271(2)	−0.0124(1)	0.7088(1)	0.019
C(11)	0.271(1)	0.0387(4)	0.7532(7)	0.018
C(12)	0.332(1)	0.0033(4)	0.7225(7)	0.012
C(13)	0.350(1)	−0.0347(4)	0.7362(8)	0.019
C(14)	0.293(2)	−0.0649(4)	0.7849(8)	0.022
O(14)	0.1647(9)	−0.0676(3)	0.7921(6)	0.027
N(11)	0.385(1)	−0.0900(3)	0.8179(7)	0.026
C(15)	0.345(2)	−0.1231(4)	0.8668(9)	0.036
C(16)	0.358(2)	−0.1141(5)	0.953(1)	0.069
C(111)	−0.024(2)	0.0190(4)	0.7469(9)	0.031(4)
O(111)	−0.106(1)	0.0010(3)	0.7116(7)	0.048
C(112)	0.123(2)	0.0114(4)	0.8857(9)	0.031(4)
O(112)	0.135(1)	−0.0102(3)	0.9384(6)	0.044
C(113)	−0.010(2)	0.0840(4)	0.8480(9)	0.035(4)
O(113)	−0.080(1)	0.1075(3)	0.8713(7)	0.046
C(121)	0.345(1)	0.1008(4)	0.6470(9)	0.024(3)
O(121)	0.435(1)	0.1126(3)	0.6114(6)	0.042
C(122)	0.083(2)	0.0710(4)	0.6241(9)	0.029(4)
O(122)	0.003(1)	0.0590(3)	0.5758(6)	0.045
C(123)	0.136(2)	0.1338(5)	0.7262(9)	0.036(4)
O(123)	0.101(1)	0.1644(3)	0.7395(6)	0.045
C(131)	0.390(2)	0.0497(4)	0.921(1)	0.034(4)
O(131)	0.423(1)	0.0340(3)	0.9793(7)	0.052
C(132)	0.511(2)	0.0887(4)	0.8029(9)	0.028(4)
O(132)	0.6195(9)	0.0950(3)	0.7861(7)	0.038
C(133)	0.286(2)	0.1215(4)	0.8795(9)	0.030(4)
O(133)	0.250(1)	0.1487(3)	0.9094(6)	0.035
C(141)	0.324(1)	0.0125(4)	0.5475(9)	0.026(4)
O(141)	0.329(1)	0.0369(3)	0.5019(6)	0.038
C(142)	0.127(2)	−0.0359(4)	0.6099(9)	0.028(4)
O(142)	0.011(1)	−0.0456(3)	0.5988(6)	0.045
C(143)	0.372(2)	−0.0691(4)	0.5760(9)	0.028(4)
O(143)	0.412(1)	−0.0962(3)	0.5469(6)	0.040
C(151)	0.603(1)	0.0248(4)	0.6491(8)	0.022(3)
O(151)	0.649(1)	0.0475(3)	0.6110(6)	0.030
C(152)	0.617(1)	0.0000(4)	0.8036(9)	0.023(3)
O(152)	0.671(1)	0.0069(3)	0.8643(6)	0.036
C(153)	0.634(1)	−0.0538(4)	0.6825(8)	0.022(3)
O(153)	0.697(1)	−0.0796(3)	0.6648(6)	0.036
Molecule 2				
Co(21)	0.6255(2)	0.2371(1)	0.6077(1)	0.025
Co(22)	0.7271(2)	0.2023(1)	0.7261(1)	0.023
Co(23)	0.8738(2)	0.2472(1)	0.6548(1)	0.021
Co(24)	0.4845(2)	0.3061(1)	0.7965(1)	0.021
Co(25)	0.7276(2)	0.3124(1)	0.8588(1)	0.023
C(21)	0.707(1)	0.2566(4)	0.7082(8)	0.018
C(22)	0.668(1)	0.2891(4)	0.7547(8)	0.020
C(23)	0.651(1)	0.3284(4)	0.7526(8)	0.018
C(24)	0.697(1)	0.3611(4)	0.7055(8)	0.022
O(24)	0.8188(9)	0.3624(3)	0.6844(6)	0.029
N(21)	0.601(1)	0.3885(3)	0.6878(6)	0.018
C(25)	0.633(1)	0.4221(4)	0.6418(8)	0.023
C(26)	0.603(2)	0.4156(5)	0.5544(9)	0.057
C(211)	0.452(2)	0.2180(4)	0.6197(9)	0.035(4)
O(211)	0.345(1)	0.2053(3)	0.6246(8)	0.060

TABLE 3 (continued)

Atom	x	y	z	U_{eq}/U_{11}
C(212)	0.583(2)	0.2828(4)	0.5665(9)	0.032(4)
O(212)	0.550(1)	0.3132(3)	0.5423(6)	0.044
C(213)	0.669(2)	0.2079(4)	0.524(1)	0.034(4)
O(213)	0.700(1)	0.1880(4)	0.4734(7)	0.058
C(221)	0.847(2)	0.1986(4)	0.814(1)	0.035(4)
O(221)	0.920(1)	0.1970(3)	0.8694(7)	0.060
C(222)	0.565(2)	0.1902(5)	0.773(1)	0.052(5)
O(222)	0.467(1)	0.1809(3)	0.7990(8)	0.062
C(223)	0.768(2)	0.1579(5)	0.6761(9)	0.036(4)
O(223)	0.796(1)	0.1296(3)	0.6428(7)	0.048
C(231)	0.896(2)	0.2897(5)	0.593(1)	0.033(4)
O(231)	0.913(1)	0.3136(3)	0.5518(6)	0.046
C(232)	1.014(2)	0.2548(4)	0.7344(9)	0.028(4)
O(232)	1.100(1)	0.2590(3)	0.7823(6)	0.049
C(233)	0.965(2)	0.2120(4)	0.5926(9)	0.028(4)
O(233)	1.018(1)	0.1899(3)	0.5576(6)	0.040
C(241)	0.427(2)	0.2677(4)	0.8615(9)	0.029(4)
O(241)	0.394(1)	0.2449(3)	0.9051(6)	0.044
C(242)	0.367(2)	0.2979(4)	0.7105(9)	0.028(4)
O(242)	0.291(1)	0.2926(3)	0.6559(6)	0.041
C(243)	0.400(2)	0.3484(4)	0.8382(9)	0.033(4)
O(243)	0.347(1)	0.3742(3)	0.8646(7)	0.054
C(251)	0.739(2)	0.2713(5)	0.925(1)	0.040(4)
O(251)	0.741(1)	0.2452(3)	0.9686(6)	0.049
C(252)	0.910(2)	0.3264(4)	0.845(1)	0.033(4)
O(252)	1.016(1)	0.3367(3)	0.8332(7)	0.044
C(253)	0.690(2)	0.3516(4)	0.9271(9)	0.029(4)
O(253)	0.666(1)	0.3760(3)	0.9699(6)	0.044

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

Acknowledgments

We thank Dr W.T. Robinson, University of Canterbury, for the data collection, Dr M.I. Liddell, University of Adelaide, for the FAB mass spectra, and the University of Otago for the award of a post-graduate scholarship (to G.H.W.).

References

1 G. H. Worth, B. H. Robinson and J. Simpson, *Organometallics, 11* (1992) 501.

2 K. M. Nicholas and R. Pettit, *J. Organomet. Chem., 44* (1972) C21; *Tetrahedron Lett.,* (1971) 3475.

3 D. Seyferth and A. T. Wehman, *J. Am. Chem. Soc., 92* (1970) 5520; D. Seyferth, M. O. Nestle and A. T. Wehman, *J. Am. Chem. Soc., 97* (1975) 7417.

4 R. S. Dickson and P. J. Fraser, *Adv. Organomet. Chem., 12* (1974) 340.

5 P. Magnus, P. Carter, J . Eliiot, R. Lewis, J. Harling, T. Pitterna, W. E. Bauta and S. Fortt, *J. Am. Chem. Soc., 114* (1992) 2544 and references therein.

6 R. J. Dellaca, B. R. Penfold, B. H. Robinson, W. T. Robinson and J. L. Spencer, *Inorg. Chem., 9* (1970) 2197.

7 R. Dolby and B. H. Robinson, *J. Chem. Soc., Dalton Trans.,* (1973) 1794.

8 G. Bor, *Symp. Coord. Chem. Tihany (Hungary),* 1964, p. 361.

9 D. M. Hoffman, R. Hoffmann, and C. R. Fisel, *J. Amer. Chem. Soc., 104* (1982) 3858.

10 D. L. Thorn and R. Hoffmann, *Inorg. Chem., 17* (1978) 126.

11 D. Gregson and J. A. K. Howard, *Acta Crystallogr., C39* (1983) 1024.

12 D. H. Farrah and N. C. Payne, *Inorg. Chem., 20* (1981) 821.

13 B. R. Penfold and B. H. Robinson, *Acc. Chem. Res., 6* (1973) 73.

14 H. G. Viehe, *Chemistry of the Acetylenes,* Marcel Dekker, New York, 1969.

15 L. I. Petersen, *Tetrahedron Lett.,* (1968) 5357.

16 S. E. Xiang, A. A. Baake, H. W. Chen, C. J. Eyermann, J. L. Hoskins, T. H. Lee, D. Seyferth, H. P. Withero and W. L. Jolly, *Organometallics, 1* (1982) 689.

17 K. M. Nicholas, M. O. Nestle, and D. Seyferth, in H. Alper (ed.), *Transition Metal Organometallics in Organic Synthesis,* Vol 2, Academic Press, New York, 1978, Chap 1.

18 D. Seyferth and C. L. Nivert, *J. Organomet. Chem., 113* (1976) C65.

19 R. D. W. Kemmitt and D. R. Russell, Cobalt, in G. Wilkinson and F. G. A. Stone (eds.), *Comprehensive Organometallic Chemistry,* Vol. 5, 1982, Chap. 34.

20 G. F. Meyers and M. B. Hall, *Organometallics, 4* (1985) 1770.

21 R. E. Gates, M. F. d'Agostino, R. E. Perrier, B. G. Sayer and M. J. McGlinchey, *Organometallics, 6* (1987) 1181.

22 Y. Iwashita, F. Tamura and H. Wakamatsu, *Bull. Chem. Soc. Japan*, *43* (1973) 1520.
23 D. Seyferth, *Adv. Organomet. Chem.*, *14* (1969) 97.
24 R. Ercoli, E. Santambrogio and G. Casagrande, *Chem. Ind. (Milan)*, *44* (1962) 1344.
25 R. N. Keller and H. D. Wycoff, *Inorg Synth.*, *2* (1946) 1.
26 R. J. Dellaca, B. R. Penfold, B. H. Robinson, W. T. Robinson and J. L. Spencer, *Inorg. Chem.*, *9* (1970) 2204.
27 *International Tables for X-ray Crystallography*, Vol. 1, Kynoch Press, Birmingham, 1966.
28 G. M. Sheldrick, SHELXTL, *An integrated system for solving, refining and displaying crystal structures from diffraction data*, University of Göttingen, 1981.
29 G. M. Sheldrick, SHELX-76, *Program for Crystal Structure Determination*, University of Cambridge, 1976.