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Five-membered OsC_3N heterocycles from osmium azavinylidenes as precursors *

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Abstract

The azavinylidene osmium complex $[(mes)Os(=N=CPh_2)(P^iPr_3)]PF_6$ (**3**; mes = 1.3.5-$C_6H_3Me_3$), which was prepared in two steps from $[(mes)OsCl_2(P^iPr_3)]$, CH_3CO_2Na/KPF_6 and $HN=CPh_2$, has been shown to react with trifluoracetic acid to give the isomeric heterocycle $[(mes)Os(NH=C(Ph)C_6H_4)(P^iPr_3)]PF_6$ (**4**) in almost quantitative yield. With CF_3CO_2D, the monodeuterated compound **4**-d_1, containing a N–D unit in the five-membered ring, is obtained. An analogue of **4** with the composition $[(mes)Os(NH=C(Ph)C_6H_4)(PMe_3)]X$ (X = PF_6 **14a**, SbF_6 **14b**) has been made both from $[(mes)Os(=N=CPh_2)(PMe_3)]PF_6$ (**12**) and CF_3CO_2H and from $[(mes)OsCl(NH=CPh_2)(PMe_3)]SbF_6$ (**13**) and CF_3CO_2Ag. The reaction of **4** with NaH or KO^tBu gives the uncharged heterocycle $[(mes)Os(N=C(Ph)C_6H_4)(P^iPr_3)]$ (**15**), while treatment of $[(mes)OsCl_2(NH=CPh_2)]$ (**19**) with NaS^tBu gives the related complex $[(mes)Os(NH=C(Ph)C_6H_4)(S^tBu)]$ (**20**). The crystal structure of **4** has been determined.

Key words: Osmium; Azavinylidene; Cyclometallation; Crystal structure; Arene complexes

1. Introduction

When we observed that vinylidene osmium complexes of the general type $[(arene)Os(=C=CHR')(PR_3)]$ are good nucleophiles and react smoothly with HX, CuX, sulfur, selenium, etc., by electrophilic addition to the osmium–carbon double bond [1], we were interested to find out whether the corresponding azavinylidene derivatives, which instead of an Os=C=CHR′ contain an Os=N=CR′R″ unit, behave analogously **. We reported recently that the compounds $[(arene)Os(=N=CR'R'')(PR_3)]X$, where arene is benzene or mesitylene, can be prepared from $[(arene)OsX_2(PR_3)]$ and either oximes or imines, and that the structures of these complexes are rather similar to that of related osmium vinylidenes [2,3]. Herein we report that the cationic azavinylidene osmium compounds $[(mes)Os(=N=CPh_2)(PR_3)]^+$ (mes = 1.3.5-$C_6H_3Me_3$), like their neutral Os=C=CHR counterparts, react with trifluoracetic acid by attack at the Os=N double bond, but that the adducts formed as intermediates are extremely labile, and undergo elimination of CF_3CO_2H to afford new five-membered osma-heterocycles.

2. Results and discussion

2.1. Preparative routes to OsC_3N heterocycles

The diphenylazavinylidene complex **3** (see Scheme 1), which was chosen for the protonation studies because of its stability was originally prepared from $[(mes)OsCl_2(P^iPr_3)]$ (**1**), $AgPF_6$ and diphenylketimine [3]. We now find that it can be made in two steps, but nevertheless in practically quantitative yield, from **1**, CH_3CO_2Na/KPF_6 and $HN=CPh_2$. In the first step, *i.e.* the preparation of the (η^2-acetato)osmium compound **2**, it is essential to use water or acetone/water 1/4 as the solvent because in polar organic media such as methanol or acetone the yield is not > 40%. The reaction of **2** with a 2.5-fold excess of diphenylketimine proceeds in CH_2Cl_2 at room temperature and, besides **3**, gives only the immonium salt $[H_2N=CPh_2](OAc)$.

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* Dedicated to Professor Akira Nakamura on the occasion of his 60th birthday in recognition of his important contributions to organometallic chemistry.

** Instead of "azavinylidene", the name "alkylideneimido" can also be used.

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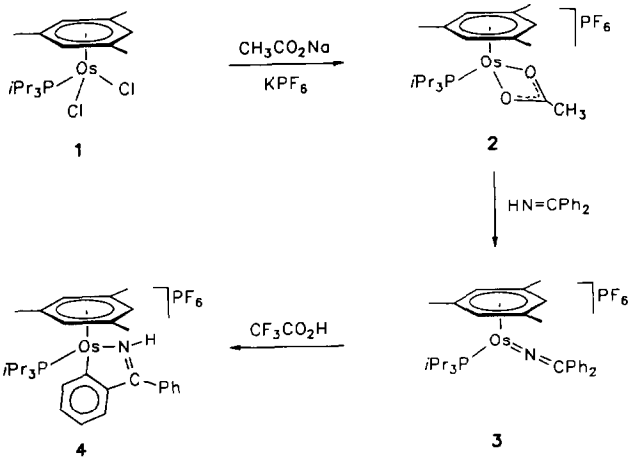
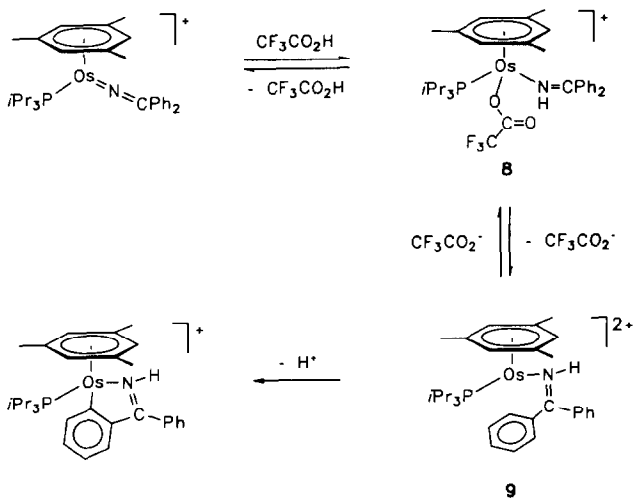


Scheme 1.

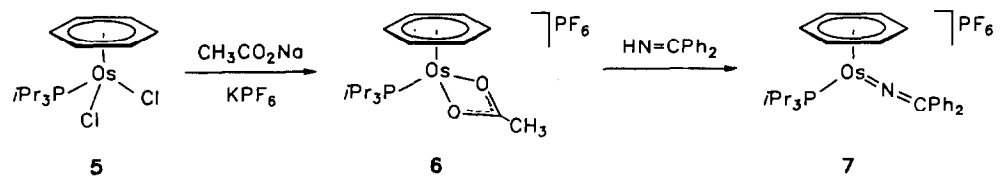


Scheme 3.

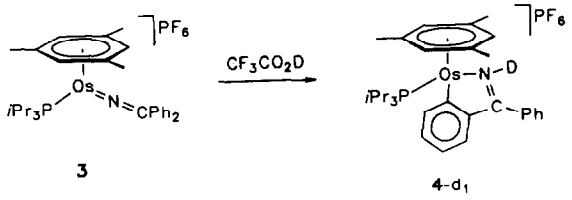
Whereas on treatment of **3** with a solution of HCl in dichloromethane complete cleavage of the Os=N bond occurs and compound **1** is obtained, reaction of **3** with an equimolar amount of CF_3CO_2H leads to the quantitative formation of the osma-heterocycle **4**. The related complex with benzene instead of mesitylene as the π-bound ring ligand has been prepared similarly [3]. The "acetate route" to yield azavinylidene osmium derivatives has also been used to prepare complex **7** (see Scheme 2), which was obtained in our previous studies from $[C_6H_6OsI_2(P^iPr_3)]$, $LiN{=}CPh_2$ and NH_4PF_6, or from $[C_6H_6OsI_2(P^iPr_3)]$, $HN{=}CPh_2$ and KPF_6 in methanol [3]. Compounds **2** and **6** are yellow air-stable solids which in their IR spectra display a $\nu(OCO)_{asym}$ band at 1485 cm^{-1} typical of a chelated (η^2-bonded) acetate ligand [4].

The mechanism of the reaction of **3** with CF_3CO_2H deserves some comment. Since the metalla-heterocycle **4** is isomeric with the azavinylidene complex **3**, the conversion of **3** into **4** would be expected to take place even with a catalytic amount of the acid, and this is indeed the case. When a solution of **3** in CH_2Cl_2 is stirred for 8 h at room temperature, compound **4** is formed in *ca.* 90% yield. Since with an equimolar amount of CF_3CO_2H, the reaction is complete in 1 h, we assume that the initial addition of the acid to the Os=N double-bound is the rate-determining step. Like the corresponding vinyl osmium derivative $[C_6H_6Os(CH{=}CHPh)(\eta^1\text{-}O_2CCF_3)(P^iPr_3)]$ [1c], the imino complex **8** (Scheme 3) probably contains a labile Os–O_2CCF_3 bond, and thus after cleavage generates a coordinatively unsaturated intermediate **9**, which reacts by attack of the electrophilic metal center on one of the phenyl groups to give the osma-heterocycle. We note that treatment of $[C_6H_6Os(=N{=}CHPh)(P^iPr_3)]SbF_6$ with CF_3CO_2H at room temperature, gives the cationic imino(trifluoracetato)osmium compound $[C_6H_6Os(\eta^1\text{-}O_2CCF_3)(HN{=}CHPh)(P^iPr_3)]^+$ as a mixture of *E*- and *Z*-isomers, both of which have been characterized by IR and ^1H NMR spectroscopy [3].

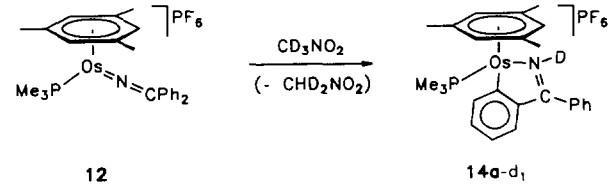
In agreement with the mechanism outlined in Scheme 3, the reaction of **3** with CF_3CO_2D affords the monodeuterated derivative **4**-d_1 (Scheme 4). With a twelve-fold excess of the acid in CH_2Cl_2 as solvent, the reaction is complete in 10 min. The finding that no H/D exchange at the NH group takes place either on treatment of **4** with CF_3CO_2D or of **4**-d_1 with CF_3CO_2H strongly supports the formation of the imino compound **8** (or **8**-d_1) as an intermediate. The deuterated complex **4**-d_1 is best characterized by the N–D stretching frequency in the IR spectrum at 2475 cm^{-1} which is shifted by 850 cm^{-1} to lower frequencies compared with that for **4**.



Scheme 2.



Scheme 4.

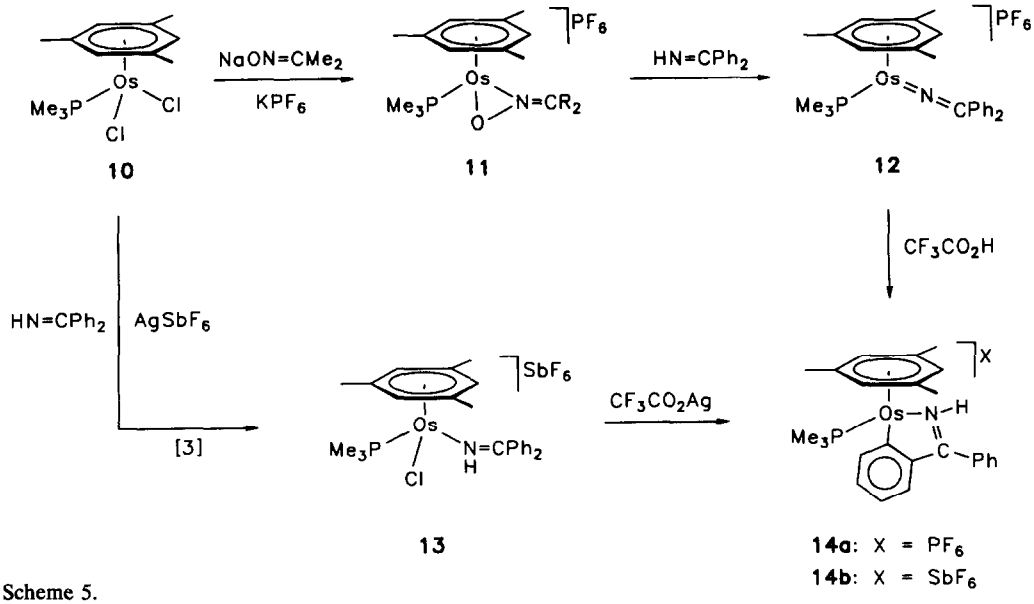


Scheme 6.

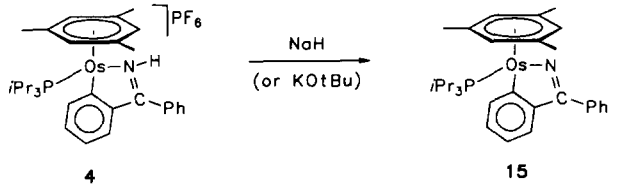
The synthesis of azavinylidene complex **12** containing PMe_3 as the phosphine ligand was not carried out by the "acetate route", but by an analogous route via the cationic oximato osmium derivative **11** as a precursor (Scheme 5). Compound **11** was obtained from $[(mes)OsCl_2(PMe_3)]$ (**10**), $NaON{=}CMe_2$ and KPF_6 and possesses similar properties to some other oximato ruthenium [5] and osmium [6] complexes. The reaction of **11** with $HN{=}CPh_2$, which leads to the displacement of the η^2-$ON{=}CMe_2$ by the $N{=}CPh_2$ ligand, proceeds under mild conditions and gives compound **12** in moderate yields. The final conversion of **12** by treatment with CF_3CO_2H into the isomeric metalla-heterocycle **14a** takes place almost quantitatively, and probably involves the intermediate formation of a cationic imine osmium species. This is confirmed by the reaction of the chloro(imino) complex **13** with CF_3CO_2Ag, which yields the SbF_6 salt **14b** of the heterocycle. An arene ruthenium derivative with a RuC_3N five-membered ring (containing, however, a phenyl group on the nitrogen and a hydrogen on the β-C-atom) was recently prepared by Boncella *et al.* [7], also by the "silver salt method", starting from $[C_6Me_6RuCl_2(PMe_3)]$, two equivalents of benzylideneaniline and two equivalents of $AgBF_4$.

The pronounced tendency of the cationic azavinylidene complex $[(mes)Os(=N{=}CPh_2)(PMe_3)]^+$ to form the isomeric osma-heterocycle is also illustrated by the observation that in CD_3NO_2 solution compound **12** is smoothly converted into the monodeuterated derivative **14a**-d_1 (see Scheme 6). The reaction is complete after 3 h at room temperature. We note that the behavior of the $[(mes)Os(=N{=}CPh_2)(PMe_3)]^+$ cation is in sharp contrast to that of the corresponding species with P^iPr_3 instead of PMe_3 as the phosphine ligand, which in CD_3NO_2 is stable for several days.

Deprotonation of the imino group of the OsC_3N heterocycle in **4** occurs upon treatment with an excess of NaH in THF or with KO^tBu in ether. The yellow crystalline compound **15** (Scheme 7), which has been fully characterized by elemental analysis as well as ^1H, ^{13}C and ^{31}P NMR spectroscopy, is moderately air-sensitive and readily soluble in non-polar solvents such as ether and pentane. The neutral complex smoothly re-



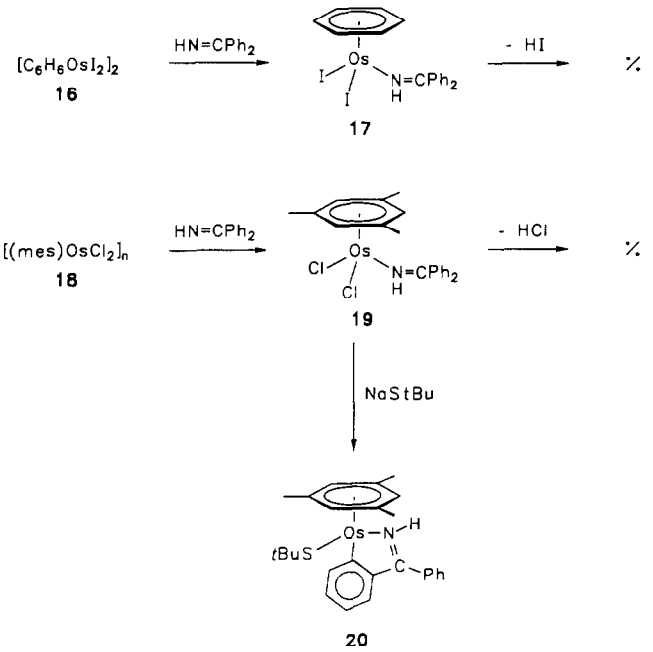
Scheme 5.



Scheme 7.

acts with acids (and slowly even with methanol) to regenerate the cation $[(mes)\overline{Os(NH{=}C(Ph)C_6H_4)}(P^iPr_3)]^+$.

All attempts to prepare an uncharged osmium azavinylidene of the general formula [(arene)Os(=N $=CPh_2)X$] with X = Cl or I were unsuccessful. The two imino complexes **17** and **19** (see Scheme 8), which are formed on treatment of the dimeric or oligomeric precursors **16** and **18**, are completely inert toward an excess of NEt_3 and do not react by HX elimination. However, with strong bases such as KO^tBu or $NaNH_2$ a reaction occurs which leads to unidentified decomposition products in addition to Bu^tOH or NH_3. We believe that the $HN{=}CPh_2$ ligand in **17** and **19** is coordinated *via* the nitrogen atom and not *via* the N=C double bond (see comparison ref. 8) mainly because the ^{13}C NMR resonance of the quaterly carbon atom appears at rather low field. Hoberg *et al.* have shown [9] that in solutions of the nickel complex [Ni $(NH{=}CPh_2)_2$] both the "side-on" and the "end-on"



Scheme 8.

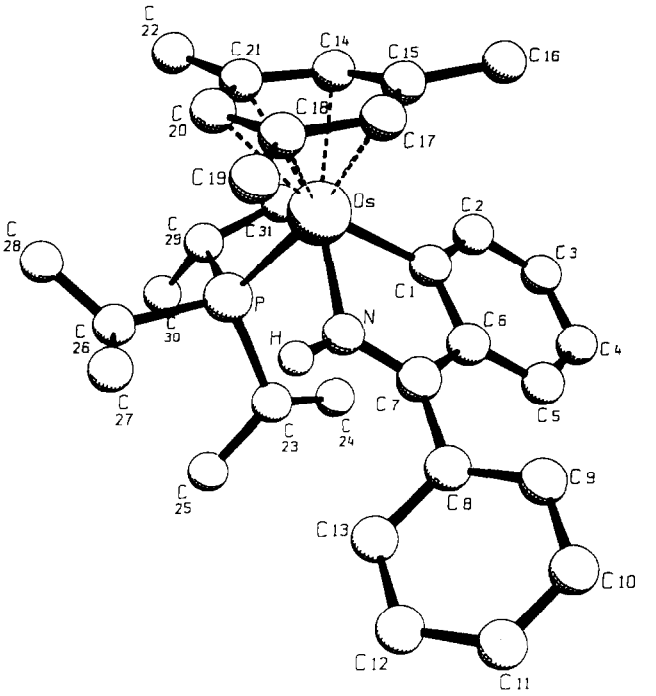


Fig. 1. Molecular structure of one enantiomer of **8** (hydrogen atoms omitted for clarity).

form are present, and differ in the chemical shift of the N=*C* carbon atom by *ca.* 100 ppm.

A neutral five-membered metalla-heterocycle of the $[(arene)\overline{Os(NH{=}C(Ph)C_6H_4)}X]$ type was obtained when a solution of **19** was treated with an equimolar amount of NaS^tBu. The yield of the red crystalline solid was *ca.* 50%; surprisingly it was not increased when a molar ratio of **19**: $NaS^tBu = 1:2$ was used. The relevant spectroscopic data for **20** (for details see experimental section) are similar to those for the cationic derivatives **4** and **14**, and thus need no further discussion.

2.2. *Molecular structure of complex 4*

A single-crystal X-ray diffraction study of compound **4** confirmed the structure suggested in Scheme 1. The SCHAKAL plot of the structure (Fig. 1) reveals that the osmium is coordinated in a pseudo-octahedral fashion, with the mesitylene ligand occupying three coordination-sites. There are two independent molecules in the unit cell and these correspond to the two enantiomers of the complex cation. The OsC_3N heterocycle (containing the carbon atoms C1, C6 and C7) is nearly planar, and the carbon atoms of the annelated ring (C2–C5) are located in the same plane. For the two independent molecules, the dihedral angle between the five- and the six-membered rings are 2.9° and 1.7°, respectively (Table 1). The phenyl group at C7 is twisted out of the OsC_3N plane by an angle of 52.5 ± 1°.

TABLE 1. Selected intramolecular bond distances (Å) and bond angles (°) in complex **4**, with esds [there are two independent molecules (molecule 1/molecule 2) in the unit cell]

Os–P1	2.386(2)/2.399(2)	C2–C3	1.39(1)/1.38(1)
Os–N	2.074(5)/2.091(5)	C3–C4	1.37(1)/1.38(1)
Os–C1	2.073(6)/2.070(6)	C4–C5	1.39(1)/1.37(1)
N–C7	1.282(8)/1.289(8)	C5–C6	1.426(9)/1.394(9)
C1–C2	1.422(9)/1.411(9)	C6–C7	1.446(9)/1.486(9)
C1–C6	1.439(8)/1.44(1)	C7–C8	1.50(1)/1.469(9)
P–Os–N	87.2(2)/86.1(1)	C3–C4–C5	120.5(7)/120.5(7)
P–Os–C1	90.6(2)/88.7(2)	C4–C5–C6	120.0(7)/119.2(8)
N–Os–C1	76.5(2)/76.1(2)	C1–C6–C5	120.4(6)/121.7(8)
Os–N–C7	119.9(5)/121.3(5)	C1–C6–C7	113.7(6)/112.9(5)
Os–C1–C2	129.3(5)/127.9(5)	C5–C6–C7	125.8(7)/125.1(7)
Os–C1–C6	114.3(4)/116.0(5)	N–C7–C6	114.7(7)/113.5(6)
C2–C1–C6	116.2(6)/116.0(6)	N–C7–C8	121.2(7)/122.9(7)
C1–C2–C3	122.0(7)/120.6(7)	C6–C7–C8	124.1(7)/123.5(6)
C2–C3–C4	120.8(8)/121.6(7)		

The Os–C1 distance is 2.07 Å, and thus differs only slightly from that of the Os–C_6H_5 bonds in the carbene complex [(mes)Os(=C(Ph)NHMe)$(C_6H_5)_2$] [10].

With regard to the delocalization of the π-electrons in the heterocyclic ring, it is important to note that although the C1–C6 and C6–C7 distances are almost identical the N–C7 bond length of 1.289(8) or 1.282(8) Å clearly supports the presence of a C–N double bond. As far as the five-membered ring is concerned, similar structural data have been obtained for $[(C_6Me_6Ru(NPh{=}CHC_6H_4)(PMe_3)]^+$ [11] and also for the uncharged rhodaindene $[C_5H_5Rh(CPh{=}CHC_6H_4)(P^iPr_3)]$ [12]. The conclusion is that an analogy in structure and bonding not only exists for metal vinylidenes $[L_nM(=C=CHR)]$ and metal azavinylidenes $[L_nM(=N=CRR')]^+$ [2,3] but also for the corresponding metallaheterocycles MC_3N and MC_4.

3. Experimental section

All reactions were carried out under argon and in carefully dried solvents. The starting materials [(mes)$OsCl_2(P^iPr_3)$] (**1**) [13], $[C_6H_6OsCl_2(P^iPr_3)]$ (**5**) [6], [(mes)$OsCl_2(PMe_3)$] (**10**) [14], [(mes)OsCl(HN=CPh_2)(PMe_3)]SbF_6 (**13**) [3], $[C_6H_6OsI_2]_2$ (**16**) [15] and [(mes)$OsCl_2]_n$ (**18**) [16] were prepared by known methods. IR: Perkin-Elmer 1420; NMR: Varian EM 360 L, Jeol FX 90 Q, Bruker AMX 400. Equivalent conductivity Λ was measured in nitromethane. Melting points were determined by differential thermal analysis.

3.1. Preparation of [(mes)Os(η^2-O_2CCH_3)(P^iPr_3)]PF_6 (2)

A suspension of 97 mg (0.18 mmol) of **1** in 5 ml of water or 5 ml of acetone/water (1/4) was treated with 35 mg (0.19 mmol) of KPF_6 and 15 mg (0.18 mmol) of CH_3CO_2Na and the mixture stirred for 1 h at room temperature. The mixture was subsequently extracted three times with 5 ml of CH_2Cl_2, and the combined extracts were taken to dryness under vacuum. The residue was dissolved in 10 ml of CH_2Cl_2, the solution was filtered, and the solvent was removed from the filtrate. Recrystallization of the residue from CH_2Cl_2/pentane gave a yellow microcrystalline solid. Yield 113 mg (93%); dec. temp. 184°C; Λ 81 $cm^2\ \Omega^{-1}\ mol^{-1}$. Anal. Found: C, 35.59; H, 5.17. $C_{20}H_{36}F_6O_2OsP_2$ calcd.: C, 35.61; H, 5.38%. IR (KBr): $\nu(OCO)_{asym}$ 1485 cm^{-1}. ^1H NMR (60 MHz, CD_3NO_2): δ 5.90 (s; 3H; $C_6H_3Me_3$), 2.53 (m; 3H; $PCHCH_3$), 2.37 (s; 9H; $C_6H_3Me_3$), 1.97 (s; 3H; CH_3CO_2), 1.33 (dd; J(PH) = 14.2, J(HH) = 7.0 Hz; 18H; $PCHCH_3$). ^{13}C NMR (22.5 MHz, CD_3NO_2): δ 194.10 (d; J(PC) = 2.6 Hz; CH_3CO_2), 98.72 (d; J(PC) = 1.7 Hz; CCH_3 of mes), 72.49 (d; J(PC) = 2.6 Hz; CH of mes), 25.17 (d; J(PC) = 27.3 Hz, $PCHCH_3$), 24.79 (s; CH_3CO_2), 19.90 (s; $PCHCH_3$), 19.75 (s; CCH_3 of mes). ^{31}P NMR (36.2 MHz, CD_3NO_2): δ 20.56 (s; P^iPr_3), −145.57 (sept; J(PF) = 707.0 Hz; PF_6).

3.2. Preparation of [(mes)Os(=N=CPh_2)(P^iPr_3)]PF_6 (3) from 2

A solution of 82 mg (0.12 mmol) of **2** in 5 ml of CH_2Cl_2 was treated with 50 μl (0.30 mmol) of $HN{=}CPh_2$ and the mixture was stirred for 45 min at room temperature. The solvent was removed and the residue recrystallized from CH_2Cl_2/ether to give an orange crystalline solid, which was identified spectroscopically as **3** by comparison with an authentic sample [3]. Yield 89 mg (93%).

3.3. Preparation of [(mes)Os(NH=C(Ph)C_6H_4)(P^iPr_3)]PF_6 (4)

A solution of 112 mg (0.14 mmol) of **3** in 3 ml of CH_2Cl_2 was treated with 11 μl (0.14 mmol) of CF_3CO_2H and the mixture was stirred for 1 h at room temperature and 25 ml of ether were then added. An orange solid separated, and was filtered off and dried in vacuum. Yield 101 mg (91%); dec. temp. 216°C; Λ 72 $cm^2\Omega^{-1}mol^{-1}$. Anal. Found: C, 47.04; H, 5.56; N, 2.04. $C_{31}H_{43}F_6NOsP_2$ calcd.: C, 46.79; H 5.45; N, 1.76%. IR (KBr): ν(NH) 3325 cm^{-1}. ^1H NMR (90 MHz, CD_3NO_2): δ 9.58 (s, br; 1H; NH), 8.25, 7.58, 7.13 (all m; 9H; C_6H_4 and C_6H_5), 5.62 (s; 3H; $C_6H_3Me_3$), 2.31 (s; 9H; $C_6H_3Me_3$), 2.24 (m; 3H; $PCHCH_3$), 1.17 (dd; J(PH) = 14.5, J(HH) = 7.3 Hz; 9H; $PCHCH_3$), 0.94 (dd; J(PH) = 13.1, J(HH) = 7.1 Hz; 9H; $PCHCH_3$). ^{13}C NMR (22.5 MHz, CD_3NO_2): δ 191.72 (d; J(PC) = 1.5 Hz; N=C), 174.62 (d; J(PC) = 11.7 Hz; OsC), 146.17, 143.83, 143.73, 136.64, 133.39,

132.38, 130.33, 129.62, 123.41 (all s; C_6H_4 and C_6H_5), 101.44 (d; $J(PC) = 2.2$ Hz; CCH_3 of mes), 82.10 (d; $J(PC) = 2.2$ Hz; CH of mes), 25.36 (d; $J(PC) = 27.1$ Hz; $PCHCH_3$), 21.15, 19.43 (both s; $PCHCH_3$), 18.59 (d; $J(PC) = 2.2$ Hz; CCH_3 of mes). ^{31}P NMR (36.2 MHz, C_3NO_2): δ 0.96 (s; P^iPr_3), −145.57 (sept; $J(PF) = 707.1$ Hz; PF_6).

3.4. Preparation of [(mes)Os(ND=C(Ph)C$_6$H$_4$)-(P^{i}Pr$_3$)]PF$_6$ (4-d$_1$)

This was made as described for **4** but from 87 mg (0.11 mmol) of **3** and 100 μl (1.31 mmol) of CF_3CO_2D. Orange-yellow crystals were isolated. Yield 78 mg (89%). IR (KBr): ν(ND) 2475 cm^{-1}.

3.5. Preparation of [C$_6$H$_6$Os(η^2-O$_2$CCH$_3$)(P^{i}Pr$_3$)]PF$_6$ (6)

A suspension of 145 mg (0.25 mmol) of **5** in 5 ml of acetone/water (1/4) was treated with 60 mg (0.33 mmol) of KPF_6 and 25 mg (0.30 mmol) of CH_3CO_2Na and the mixture was stirred for 1 h at room temperature. Worked up as described for **2** a yellow microcrystalline solid. Yield 139 mg (76%); dec. temp. 179°C; Λ 73 $cm^2\ \Omega^{-1}mol^{-1}$. Anal. Found: C, 32.49; H, 4.58. $C_{17}H_{30}F_6O_2OsP_2$ calcd.: C, 32.28; H, 4.78%. IR (KBr): $\nu(OCO)_{asym}$ 1485 cm^{-1}. ^1H NMR (60 MHz, CD_3NO_2): δ 6.37 (s; 6H; C_6H_6), 2.50 (m; 3H $PCHCH_3$), 1.87 (s; 3H; CH_3CO_2), 1.30 (dd; $J(PH) = 14.4$, $J(HH) = 7.1$ Hz; 18H; $PCHCH_3$). ^{13}C NMR (22.5 MHz, CD_3NO_2): δ 194.89 (d; $J(PC) = 2.2$ Hz; CH_3CO_2), 78.16 (d; $J(PC) = 2.2$ Hz; C_6H_6), 26.42 (d; $J(PC) = 27.8$ Hz; $PCHCH_3$), 24.53 (s; CH_3CO_2), 19.82 (s; $PCHCH_3$). ^{31}P NMR (36.2 MHz, CD_3NO_2): δ 23.90 (s; P^iPr_3), −144.37 (sept; $J(PF) = 707.5$ Hz; PF_6).

3.6. Preparation of [C$_6$H$_6$Os(=N=CPh$_2$)(P^{i}Pr$_3$)]PF$_6$ (7) from 6

A solution of 102 mg (0.16 mmol) of **6** in 5 ml of CH_2Cl_2 was treated with 50 μl (0.30 mmol) of $HN{=}CPh_2$ and the mixture stirred for 45 min at room temperature. Work-up as described for **3** gave orange crystals, which were identified spectroscopically as **7** by comparison with an authentic sample [3]. Yield 115 mg (95%).

3.7. Preparation of [(mes)Os(η^2-ON=CMe$_2$)(PMe$_3$)]PF$_6$ (11)

A solution of 91 mg (0.20 mmol) of **10** in 5 ml of methanol was treated with 40 mg (0.22 mmol) of KPF_6 and 25 mg (0.26 mmol) of $NaON{=}CMe_2$ and the mixture was stirred for 30 min at room temperature. The solvent was removed, the residue extracted with 20 ml of CH_2Cl_2, and the extract concentrated *in vacuo* to *ca.* 1 ml. The solution was then chromatographed on Al_2O_3 (neutral, activity grade V, height of column 2 cm). A yellow fraction was eluted with CH_2Cl_2, and removal of the solvent left a yellow air-sensitive oil. Yield 42 mg (35%). ^1H NMR (60 MHz, CD_3NO_2): δ 5.78 (s; 3H; $C_6H_3Me_3$), 2.43 (s; 9H; $C_6H_3Me_3$), 2.18, 2.12 (both s; 6H; $N{=}CCH_3$), 1.37 (d; $J(PH) = 10.6$ Hz; 9H; PCH_3). ^{31}P NMR (36.2 MHz, CD_3NO_2): δ −28.65 (s; PMe_3), −144.37 (sept; $J(PF) = 707.5$ Hz; PF_6).

3.8. Preparation of [(mes)Os(=N=CPh$_2$)(PMe$_3$)]PF$_6$ (12)

The reaction of **10** (95 mg, 0.21 mmol), KPF_6 (50 mg, 0.27 mmol) and $NaON{=}CMe_2$ (30 mg, 0.32 mmol) was carried out as described for **11**, but the yellow fraction eluted with CH_2Cl_2 was immediately treated with 100 μl (0.60 mmol) of $HN{=}CPh_2$. The mixture was stirred for 1 h at room temperature, the solvent was removed, and the residue recrystallized from CH_2Cl_2/ether to give orange-red crystals. Yield 67 mg (30%); dec. temp. 106°C; Λ 72 $cm^2\Omega^{-1}mol^{-1}$. Anal. Found: C, 41.96; H, 4.36; N, 1.86. $C_{25}H_{31}F_6NOsP_2$ calcd.: C, 42.19; H, 4.39; N, 1.97%. ^1H NMR (60 MHz, CD_3NO_2): δ 7.47 (m; 10H; C_6H_5), 6.13 (s; 3H; $C_6H_3Me_3$), 2.62 (s; 9H; $C_6H_3Me_3$), 1.53 (d; $J(PH) = 10.6$ Hz; 9H; PCH_3). ^{31}P NMR (36.2 MHz, CD_3NO_2): δ −31.58 (s; PMe_3), −144.35 (sept; $J(PF) = 707.3$ Hz; PF_6).

3.9. Preparation of [(mes)Os(NH=C(Ph)C$_6$H$_4$)-(PMe$_3$)]PF$_6$ (14a)

A solution of 206 mg (0.30 mmol) of **12** in 5 ml of CH_2Cl_2 was treated with 25 μl (0.33 mmol) of CF_3CO_2H and the mixture was stirred for 1 h at room temperature. The solvent was removed, the residue was washed twice with 5 ml of ether, and then recrystallized from CH_2Cl_2/ether to give an orange-yellow solid. Yield 189 mg (89%); dec. temp. 186°C; Λ 76 $cm^2\Omega^{-1}mol^{-1}$. Anal. Found: C, 42.45; H, 4.57; N, 1.98. $C_{25}H_{31}F_6NOsP_2$ calcd.: C, 42.19; H, 4.39; N, 1.97%. IR (KBr): ν(NH) 3310 cm^{-1}. ^1H NMR (60 MHz, CD_3NO_2): δ 10.07 (s, br; 1H; NH), 7.93, 7.57, 7.13 (all m; 9H; C_6H_4 and C_6H_5), 5.43 (s; 3H; $C_6H_3Me_3$), 2.32 (s; 9H; $C_6H_3Me_3$), 1.20 (d; $J(PH) = 10.3$ Hz; 9H; PCH_3). ^{31}P NMR (36.2 MHz, CD_3NO_2): δ −38.76 (s; PMe_3), −144.42 (sept; $J(PF) = 707.6$ Hz; PF_6).

3.10. Preparation of [(mes)Os(NH=C(Ph)C$_6$H$_4$)-(PMe$_3$)]SbF$_6$ (14b)

A solution of 117 mg (0.14 mmol) of **13** in 10 ml of CH_2Cl_2 was treated with 31 mg (0.14 mmol) of CF_3CO_2Ag and the mixture was stirred for 1.5 h at room temperature then filtered through cellulose. The filtrate was taken to dryness in vacuum, and the residue recrystallized from CH_2Cl_2/ether to give an orange-yellow solid. Yield 93 mg (83%); dec. temp. 140°C; Λ 74 $cm^2\Omega^{-1}mol^{-1}$. IR (KBr): ν(NH) 3315 cm^{-1}. ^1H

NMR (90 MHz, CD_3NO_2): δ 10.05 (s; br; 1H; NH), 7.96, 7.60, 7.17 (all m; 9H; C_6H_4 and C_6H_5), 5.45 (s; 3H; $C_6H_3Me_3$), 2.37 (s; 9H; $C_6H_3Me_3$), 1.23 (d; J(PH) = 10.3 Hz; 9H; PCH_3). ^{13}C NMR (22.5 MHz, CD_3NO_2): δ 190.57 (d; J(PC) = 2.2 Hz; N=C), 173.54 (d; J(PC) = 14.7 Hz; OsC), 146.17, 141.52, 141.39, 132.80, 132.28, 132.18, 130.33, 129.52, 129.45, 123.50 (all s; C_6H_4 and C_6H_5), 136.87 (d; J(PC) = 1.5 Hz; one C of C_6H_4 or C_6H_5), 101.28 (d; J(PC) = 2.2 Hz; CCH_3 of mes), 81.89 (d; J(PC) = 2.9 Hz; CH of mes), 19.36 (s; CCH_3 of mes), 15.90 (d; J(PC) = 38.8 Hz; PCH_3). ^{31}P NMR (36.2 MHz, CD_3NO_2): δ −38.97 (s; PMe_3).

3.11. Reaction of ***12*** *with* CD_3NO_2

A solution of 59 mg (0.08 mmol) of **12** in 0.3 ml of CD_3NO_2 was stirred for 3 h at room temperature. The solvent was then removed and the residue recrystallized from CH_2Cl_2/ether to give an orange-yellow microcrystalline solid. Yield 53 mg (93%) of $[(mes)\overline{Os(ND{=}C(Ph)}\overline{C_6H_4)}(P^iPr_3)]PF_6$ (**14a**-d_1). IR (KBr): ν(ND) 2450 cm^{-1}.

3.12. Preparation of $[(mes)\overline{Os(N{=}C(Ph)}\overline{C_6H_4)}(P^iPr_3)]$ ***(15)***

(i) A suspension of 159 mg (0.20 mmol) of **4** in 5 ml of THF was treated with 20 mg (0.83 mmol) of NaH and the mixture was stirred for 5 min at room temperature. The solvent was then removed, and the residue extracted with 20 ml of pentane. The extract was concentrated in vacuum to *ca.* 2 ml and then kept at −78°C. Small yellow crystals separated and were filtered off, washed with pentane (−30°C) and dried in vacuum. Yield 114 mg (88%); m.p. 126°C (dec.). (ii) As described for (i) but starting from 113 mg (0.14 mmol) of **14** and 70 mg (0.62 mmol) of KO^tBu in ether solution gave a yield of 77 mg (85%). Anal. Found: C, 57.39; H, 6.67; N, 2.00. $C_{31}H_{42}NOsP$ calcd.: C, 57.30; H, 6.51; N, 2.16%. ^1H NMR (400 MHz, C_6D_6): δ 8.15, 7.86, 7.63, 7.45, 7.30 (all m; 9H; C_6H_4 and C_6H_5), 4.88 (s; 3H; $C_6H_3Me_3$), 2.29 (m; 3H; $PCHCH_3$), 2.11 (s; 9H; $C_6H_3Me_3$), 1.33 (dd; J(PH) = 13.3, J(HH) = 7.3 Hz; 9H; $PCHCH_3$), 1.02 (dd; J(PH) = 12.2, J(HH) = 7.2 Hz; 9H; $PCHCH_3$). ^{13}C NMR (100.6 MHz, C_6D_6): δ 178.80 (s; N=C), 171.10 (d; J(PC) = 13.1 Hz; OsC), 155.74, 144.89 (both s; *ipso*-C of C_6H_4 and C_6H_5), 141.19, 141.17, 128.17, 128.01, 126.58, 125.85, 125.05, 121.00 (all s, C_6H_4 and C_6H_5), 95.26 (s; CCH_3 of mes), 79.41 (s CH of mes), 24.15 (d; J(PC) = 25.3 Hz; $PCHCH_3$), 20.83, 18.60 (both s; $PCHCH_3$), 18.57 (s, CCH_3 of mes). ^{31}P NMR (36.2 MHz, C_6D_6): δ −0.04 (s; PMe_3).

3.13. Preparation of $[C_6H_6OsI_2(NH{=}CPh_2)]$ ***(17)***

A suspension of 532 mg (0.51 mmol) of **16** in 20 ml of CH_2Cl_2 was treated with 0.6 ml (3.60 mmol) of $HN{=}CPh_2$ and the mixture stirred for 3 h at room temperature then filtered. The filtrate was concentrated to *ca.* 10 ml in vacuum, and 30 ml of pentane was added. The solution was cooled to 0°C and the orange solid that separated was filtered off, washed with ether and pentane, and dried in vacuum. Yield 661 mg (92%); dec. temp. 131°C. Anal. Found: C, 32.93; H, 2.39; N, 2.13. $C_{19}H_{17}I_2NOs$ calcd.: C, 32.44; H, 2.44; N, 1.99%. IR (KBr); ν(NH) 3225 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ 11.00 (s, br; 1H; NH), 7.62 (m; 10H; C_6H_5), 5.58 (s; 6H; C_6H_6). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 182.10 (s; N=C), 136.54, 136.48, 132.39, 130.63, 129.17, 128.63, 128.47, 128.14 (all s; C_6H_5), 76.21 (s; C_6H_6).

3.14. Preparation of $[(mes)OsCl_2(NH{=}CPh_2)]$ ***(19)***

This was made as described for **17**, but from 336 mg (0.44 mmol for n = 2) of **18** and 0.4 ml (2.39 mmol) of $HN{=}CPh_2$. A yellow microcrystalline solid was obtained. Yield 468 mg (95%); dec. temp. 170°C. Anal. Found: C, 46.71; H, 4.07; N 2.48. $C_{22}H_{23}Cl_2NOs$ calcd.: C, 46.92; H, 4.12; N, 2.49%. IR (KBr): ν(NH) 3215 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ 10.80 (s, br; 1H; NH), 8.11, 7.48 (both m; 10H; C_6H_5), 4.90 (s; 3H; $C_6H_3Me_3$), 2.13 (s, 9H; $C_6H_3Me_3$).

3.15. Preparation of $[(mes\overline{Os(NH{=}C(Ph)}\overline{C_6H_4)}(S^tBu)]$ ***(20)***

A suspension of 37 mg (0.33 mmol) of NaS^tBu in 10 ml of acetonitrile was treated with 185 mg (0.33 mmol) of **19** and the mixture was stirred for 1.5 h at room temperature. The solvent was then distilled off, and the residue was extracted with 20 ml of CH_2Cl_2. The extract was concentrated in vacuum to *ca.* 1 ml and then chromatographed on Al_2O_3 (neutral, activity grade V, height of column 4 cm). A red fraction was eluted with CH_2Cl_2, and removal of the solvent left an oily residue, which was recrystallized from pentane (25°C... −78°C) to give a red microcrystalline solid. Yield 104 mg (54%); m.p. 190°C (dec.). Anal. Found.: C, 53.54; H, 5.30; N, 2.40. $C_{26}H_{31}NOsS$ calcd.: C, 53.86; H, 5.39; N, 2.42%. IR (KBr): ν(NH) 3220 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ 9.48 (s, br; 1H; NH), 8.00, 7.47, 6.95 (all m; 9H; C_6H_4 and C_6H_5), 4.90 (s; 3H; $C_6H_3Me_3$), 2.20 (s; 9H; $C_6H_3Me_3$), 1.00 (s; 9H; $SCCH_3$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 185.05 (s; N=C), 179.87 (s; OsC), 143.85, 140.24, 137.14, 129.68, 129.54, 129.49, 128.48, 128.25, 120.38 (all s; C_6H_4 and C_6H_5), 94.15 (s; CCH_3 of mes), 75.96 (s; CH of mes), 38.61 (s; $SCCH_3$), 35.76 (s; $SCCH_3$), 18.81 (s; CCH_3 of mes).

3.16. Crystal structure analysis of ***4***

Single crystals were grown from CH_2Cl_2/pentane. Crystal data: Orthorhombic space group $Pca2_1$ (No.

TABLE 2. Positional parameters for complex **4**, with esds [the atoms marked with an asterisk belong to the independent molecule 2 in the unit cell] [a]

Atom	x	y	z	B_{eq}
Os*	0.74569(2)	0.38689(2)	0.957	2.907(7)
Os	0.17423(2)	0.18505(2)	0.49947(4)	2.746(6)
P1	0.2536(2)	0.0970(1)	0.4588(3)	3.05(5)
P1*	0.8564(2)	0.3247(2)	0.9357(2)	3.00(6)
P2*	0.5424(3)	0.5605(2)	0.6685(3)	6.0(1)
P2	0.4743(3)	−0.0504(3)	1.1967(4)	8.0(1)
F1*	0.5706(8)	0.4894(6)	0.6767(9)	12.7(4)
F1	0.451(1)	−0.057(1)	1.280(1)	17.0(7)
F2*	0.5109(9)	0.6314(6)	0.6571(8)	13.0(4)
F2	0.481(2)	−0.027(1)	1.121(1)	28(1)
F3*	0.578(1)	0.5645(8)	0.5907(8)	17.1(5)
F3	0.421(1)	0.009(1)	1.197(1)	26.3(7)
F4*	0.513(1)	0.5597(7)	0.7508(7)	14.8(5)
F4	0.532(1)	−0.009(1)	1.224(2)	26.2(9)
F5*	0.4729(9)	0.532(1)	0.639(1)	22.2(8)
F5	0.523(1)	−0.1037(8)	1.205(3)	30(1)
F6*	0.611(1)	0.589(1)	0.701(1)	21.7(8)
F6	0.417(1)	−0.100(1)	1.186(1)	23.0(7)
N*	0.7258(5)	0.3195(5)	1.0454(6)	3.3(2)
N	0.2564(6)	0.2131(4)	0.5743(5)	3.0(2)
C1*	0.6879(6)	0.3099(7)	0.9058(7)	3.2(2)
C1	0.2348(6)	0.2545(5)	0.4383(6)	2.9(2)
C2*	0.6674(7)	0.3041(7)	0.8290(7)	4.2(3)
C2	0.2250(8)	0.2772(7)	0.3626(8)	4.4(3)
C3*	0.6300(7)	0.2483(8)	0.8035(8)	4.7(3)
C3	0.2705(8)	0.3253(7)	0.3303(9)	5.1(3)
C4*	0.6080(8)	0.1981(8)	0.8525(9)	5.2(3)
C4	0.3249(9)	0.3554(7)	0.372(1)	5.5(4)
C5*	0.6271(7)	0.2002(6)	0.9274(8)	4.0(3)
C5	0.3371(7)	0.3366(7)	0.4466(8)	4.4(3)
C6*	0.6636(6)	0.2565(6)	0.9552(8)	3.4(2)
C6	0.2921(6)	0.2866(6)	0.4810(6)	3.3(3)
C7	0.2989(7)	0.2622(6)	0.5579(8)	3.5(3)
C7*	0.6879(6)	0.2656(6)	1.0349(7)	3.2(2)
C8*	0.6744(7)	0.2163(6)	1.0951(7)	3.2(2)
C8	0.3528(7)	0.2888(7)	0.6143(7)	3.8(3)
C9*	0.6055(8)	0.1903(8)	1.1076(9)	5.0(3)
C9	0.3572(9)	0.3552(8)	0.630(1)	5.4(4)
C10*	0.5966(8)	0.1419(7)	1.1629(9)	5.0(3)
C10	0.4048(9)	0.3784(9)	0.6846(9)	6.6(4)
C11*	0.6545(8)	0.1187(7)	1.2035(9)	4.4(3)
C11	0.4447(8)	0.335(1)	0.726(1)	7.6(5)
C12*	0.7240(7)	0.1435(7)	1.1913(8)	4.2(3)
C12	0.4414(8)	0.2673(9)	0.712(1)	6.0(4)
C13	0.3948(7)	0.2427(8)	0.6562(8)	4.5(3)
C13*	0.7338(7)	0.1914(6)	1.1371(8)	3.7(3)
C14	0.0909(7)	0.2495(8)	0.5592(9)	4.7(3)
C14*	0.6614(6)	0.4601(5)	1.000(1)	4.5(3)
C15*	0.653(1)	0.4578(7)	0.919(1)	5.5(4)
C15	0.0744(7)	0.2511(7)	0.4808(8)	4.4(3)
C16*	0.5810(9)	0.4457(9)	0.885(1)	6.5(5)
C16	0.0665(9)	0.3191(8)	0.442(1)	7.2(4)
C17	0.0661(7)	0.1910(7)	0.4415(7)	4.1(3)
C17*	0.7195(8)	0.4702(7)	0.8769(9)	4.5(3)
C18	0.0658(6)	0.1284(8)	0.4778(8)	4.9(4)
C18*	0.7869(8)	0.4877(6)	0.911(1)	4.6(3)
C19*	0.8500(8)	0.5107(7)	0.8614(9)	4.9(3)
C19	0.0442(8)	0.0655(8)	0.438(1)	6.0(4)
C20*	0.7918(7)	0.4909(6)	0.9936(9)	4.4(3)
C20	0.0796(6)	0.1278(7)	0.5573(9)	4.6(3)
C21*	0.7304(7)	0.4741(6)	1.037(1)	4.8(3)
C21	0.0951(7)	0.1865(8)	0.5980(7)	4.1(3)
C22*	0.736(1)	0.4729(8)	1.126(1)	6.3(4)
C22	0.1124(9)	0.188(1)	0.6819(9)	6.2(4)
C23	0.3524(6)	0.1224(6)	0.4488(8)	3.8(3)
C23*	0.8477(6)	0.2311(5)	0.9506(8)	3.4(2)
C24	0.3716(8)	0.1563(8)	0.3736(9)	5.0(3)
C24*	0.9133(7)	0.1931(7)	0.9819(7)	4.5(3)
C25*	0.8195(8)	0.1940(7)	0.8784(9)	4.6(3)
C25	0.4113(8)	0.0688(8)	0.466(1)	6.1(4)
C26	0.258(1)	0.0254(7)	0.5279(9)	5.3(3)
C26*	0.9316(6)	0.3450(6)	1.006(1)	4.1(3)
C27	0.273(1)	0.0486(8)	0.6095(9)	6.6(5)
C27*	0.9710(7)	0.4110(7)	0.9874(9)	4.7(3)
C28*	0.9033(8)	0.3424(9)	1.086(1)	5.6(4)
C28	0.203(1)	−0.0270(9)	0.527(1)	10.8(6)
C29	0.2246(8)	0.0540(8)	0.3669(8)	4.9(3)
C29*	0.9019(7)	0.3382(7)	0.8421(7)	3.7(3)
C30*	0.8516(9)	0.3352(7)	0.7750(9)	4.7(3)
C30	0.280(1)	0.0027(9)	0.3359(9)	7.3(4)
C31*	0.9707(8)	0.2952(7)	0.832(1)	5.3(4)
C31	0.2026(9)	0.1056(8)	0.3046(8)	5.1(4)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$.

29), $a = 18.244(2)$ Å, $b = 19.929(2)$ Å, $c = 7.649(2)$ Å, $V = 6417$ Å^3, $Z = 8$, $d_{calcd} = 1.68$ g cm^{-3}, $\mu(\mathrm{Mo}K_\alpha) = 41.3$ cm^{-1}. Crystal size $0.4 \times 0.3 \times 0.3$ mm^3. Enraf Nonius CAD4 diffractometer, MoK_α radiation (0.70930 Å), graphite monochromator, zirconium filter (factor 16.55), $T = 293$ K, $\omega/2\Theta$ scan, max. $2\Theta = 52°$; 6916 reflections were measured, 4914 were regarded as being observed [$F_o > 3\sigma(F_o)$]; intensity data were corrected for Lorentz and polarization effects, empirical absorption correction (Ψ-scan method) was applied, minimum transmission was 85.3%. The structure was solved by Direct methods (SHELXS-86); atomic coordinates (Table 2) and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares (738 parameters, unit weights, Enraf-Nonius SDP) [17]. The hydrogen atoms were placed in calculated positions (distance C–H = 0.95 Å) and the hydrogen atoms considered only for the calculation of F_c. There are two independent molecules in the unit cell which differ slightly in respect of bond distances and bond angles (Table 1). $R = 0.032$, $R_w = 0.036$ (for preferred hand); reflex/parameter ratio 6.7; residual electron density $+0.61/-0.60$ eÅ^{-3}. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftliche-technische Information mbh, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-57861, the names of the authors, and the journal citation.

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