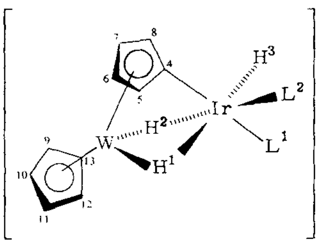
Cation *(3a)* is produced *in situ* as previously described for the formation of *(3b)* and *(3c)*[2].



PF_6 *(1a)*, L = PEt_3

$[WH_2(\eta^5\text{-}C_5H_5)_2]$
(2)

$[IrH_2L_2(EtOH)_2]PF_6$
(3a), L = PEt_3; *(3b)*, L = $PMePh_2$;
(3c), L = PPh_3

Compound *(1a)* is a green solid and is stable in air for several days. It is moderately soluble only in polar organic solvents and the solutions obtained decompose rapidly in the presence of oxygen.

Support for the proposed structure for *(1a)* stems from its ^1H-, ^{13}C- and ^{31}P-NMR spectra (in CD_2Cl_2):

^1H-NMR: $\delta = -17.57$ [H1, $^2J(H1,H2) = 3.7$ Hz, $^1J(W,H1) = 95.2$ Hz]; -18.86 [H2, $^2J(H1,H2) = {}^2J(H2,H3) = {}^2J(H2,P1) = 3.7$ Hz, $^2J(H2,P2) = 47.6$ Hz, $^1J(W,H2) = 92.4$ Hz]; -23.78 [H3, $^2J(H3,P1)$, $^2J(H3,P2) = 16.8$, 28.4 Hz]; 6.42 [(1H), 6.36 (1H), 5.09 (2H), H5—H8, 5.34 (5H), H9—H13; ^{13}C-NMR: $\delta = 85.5$ [C9—C13]; 110.3 [C4, $^2J(P1,C4) = 84.2$ Hz, $^2J(P2,C4) = 8.3$ Hz]; 95.1 [C5 or C8, $^3J(P1,C) = 7.4$ Hz]; 93.6 [C8 or C5, $^3J(P1,C) = 5.5$ Hz]; 91.2 [C6 or C7]; 89.9 [C7 or C6]; 20.3, 19.8, [PCH_2, $^1J(P,C) = 25$ Hz]; 8.0, 7.8 [PCH_2CH_3]. ^{31}P-NMR: $\delta = 6.2$ [P1, $^2J(P1,P2) = 11.8$ Hz]; 4.7 [P2].

The $^{31}P\{^1H\}$-NMR spectrum of the two non-equivalent tertiary phosphorus atoms appears as an AB pattern. The magnitude of $^2J(P1,P2)$ is consistent with a *pseudo-cis*-orientation of the phosphorus atoms. The ^1H-NMR spectrum between $\delta = -17$ and -24 ppm comprises three groups of resonances, which may be assigned to H1, H2 and H3. The two lower field signals are assigned to H1 and H2 since they show ^{183}W-satellites (natural abundance of $^{183}W = 14.3\%$) with $J(W,H) \approx 90$ Hz, consistent with one-bond interactions. Reported $^1J(W,H)$ values in related complexes are 107 Hz for *(4)*[3] and 60.3 and 59.7 Hz for *(5a)* and *(5b)*[4] respectively. A further relatively large splitting of the H2 signal stems from P2, and hence it can be concluded that these two atoms occupy a *pseudo-trans* arrangement. H3 couples to two *cis*-phosphorus atoms and H1 but, interestingly, the *trans*-coupling $^2J(H1,H3)$ is quite small (< 1.5 Hz).

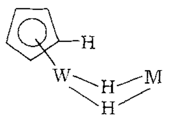
$[(\eta^5\text{-}C_5H_5)_2W(\mu\text{-}H)_2Rh(PPh_3)_2]PF_6$ *(4)*
$[(\eta^5\text{-}C_5H_5)_2W(\mu\text{-}H)_2PtR(PEt_3)_2]BF_4$ *(5a)*, R = H
(5b), R = C_6H_5

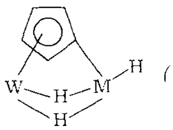
The assignment of C5 and C8 in the $^{13}C\{^1H\}$-NMR spectrum follows from the suggestions of *Davison* and *Wreford*[5], while the signal at $\delta = 110.3$ may be assigned on the basis of its position[6], spin-lattice relaxation time and ^{31}P coupling pattern.

Complex *(1a)* appears to be a member of a general class of compounds of type *(1)*; *(1b)* and *(1c)* can be prepared in a similar way to *(1a)* (L = PMe_2Ph or $PMePh_2$).

To our knowledge, the complexes of type *(1)* are the first examples of compounds containing both "$C_5H_4^{2-}$" and "H^-" bridging ligands. Although (η^5:η^1-C_5H_4) bridges have been observed in complexes of zirconium[6], molybdenum and tungsten[7,8], when bridging hydrides are present[5,8], the cyclopentadienyl moiety is present as a bridging η^5:η^5-fulvalene.

The mechanistic pathway leading to *(1)* is likely to involve the initial formation of $[(\eta^5\text{-}C_5H_5)_2W(\mu\text{-}H)_2\text{-}Ir(PEt_3)_2]^+$, which is analogous to *(4)* and contains the structural unit *(A)*, followed by the oxidative addition of a

(A)




(B)

cyclopentadienyl C—H bond, resulting in the formation of structural unit *(B)*. (Hydrogen-abstraction reactions occur easily and often irreversibly in Ir^I complexes[9].) A species of type *(B)* (M = Rh) has been postulated to explain the H/D-exchange observed in compound *(4)*[3].

Experimental

A vigorously stirred deep-red suspension of $[Ir(cod)(PEt_3)_2]PF_6$ (0.539 g, 0.79 mmol) (cod = 1,5-cyclooctadiene) in 25 mL EtOH at 0 °C was treated with H_2 for 15 min. A solution of *(2)* (0.250 g, 0.79 mmol) in 15 mL EtOH was added to the resulting clear pale-yellow solution and stirring continued for an additional 0.5 h. Solvent was evaporated (with cooling) until precipitation began and this was followed by rewarming to room temperature and subsequent recrystallization at −22°. The green microcrystalline *(1a)* formed was recrystallized again from EtOH to afford the product: yield 0.218 g (31%).

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Double Ring-Opening of Bicyclic Oxaziridines to *N*-(3-Oxopropyl)amides by Iron(II) Sulfate

By *David St. C. Black* and *Lynn M. Johnstone*[*]

Dedicated to Professor Siegfried Hünig on the occasion of his 60th birthday

Iron(II) sulfate has been shown to cleave *C*-alkyl-, *C*-aryl-[1,2] and *C*-cyano-[3] substituted oxaziridines, the nature of the products depending on the particular substitution pattern. We now report that oxaziridines of type *(2)*,

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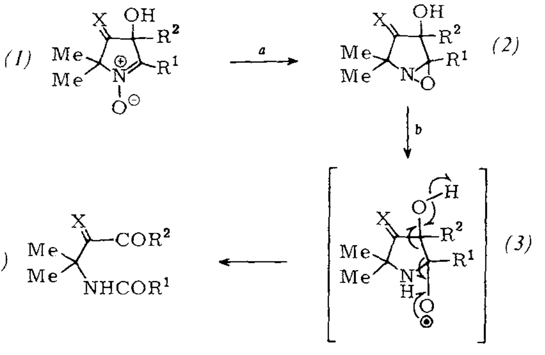
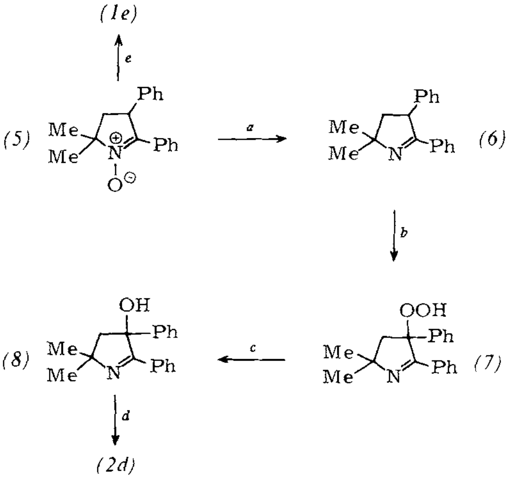
whose *C*-hydroxymethylene substituents form part of a pyrrolidine ring, undergo a reaction with iron(II) sulfate which results in opening of both rings to afford the oxoamides *(4)* (Scheme 1). An isolated example of a similar reaction which has, however a different outcome, has been previously reported by *Bischoff*[4].



(1)–(4)	X	R¹	R²
a	H, H	*t*Bu	Me
b	H, H	Ph	Me
c	H, H	Ph	Et
d	H, H	Ph	Ph
e	O	Ph	Ph

Scheme 1. *a)*: hv, benzene, 1–12 h. *b)*: $FeSO_4$, aqueous EtOH, 2 h.

The oxaziridines *(2a–e)* are formed as isomeric mixtures by photorearrangement ($\lambda_{max}=254$ or 300 nm, benzene) of the related cyclic nitrones *(1a–e)*. The known nitrones *(1a–d)*[5] can be prepared by Grignard reactions from the corresponding 3-oxo-derivatives. However, oxaziridine *(2d)* is more readily available from the method shown in Scheme 2. It is noteworthy that, on attempted recrystallization from hexane in air, the 1-pyrroline *(6)* was rapidly transformed into the stable hydroperoxide *(7)*. Unlike the 3*H*-indolyl hydroperoxides[6], *(7)* did not undergo thermal CC-bond cleavage, but afforded the alcohol *(8)* in low yield. Yields were improved by addition of triethyl phosphite. Peracid oxidation of *(8)* yielded isomerically pure *(2d)* (with *cis*-phenyl groups). – The 4-oxonitrone *(1e)* ($\nu_{max}=1776$ cm^{-1} (CO)) can be prepared in 36% yield as shown in Scheme 2.



Scheme 2. *a:* $Fe(CO)_5$/*n*Bu_2O, reflux, 24 h. *b:* O_2, hexane, reflux, 2 h. *c:* $(EtO)_3P$, tetrahydrofuran, room temperature, 1 h. *d:* 2% CH_3CO_3H in CH_3CO_2H, room temperature, 16 h. *e:* HNO_3, CH_3CN, reflux, 1 h.

The oxoamides *(4)* show infrared absorptions characteristic of the ketone and amide groups. Some other physical data are presented in Table 1.

Table 1. Selected physical data of compounds *(4)*, *(7)* and *(8)*.

Cpd.	Yield [%]	M.p. [°C]	¹H-NMR ($CDCl_3$), δ-values *gem*-Me_2	—CH_2—
(4a)	92 [a]	54–55	1.40	2.92
(4b) [7]	88 [a]	98–100	1.53	3.00
(4c)	83 [a]	[e]	1.53	2.95
(4d)	50 [b]	82–84	1.63	3.51
(4e)	55 [a]	135–136	1.77	–
(7)	74 [c]	139–142	1.28, 1.41 [f]	2.10, 2.90 ($J_{AB}=14$ Hz)
(8)	74 [d]	147–148	1.40, 1.47	2.33

[a] From nitrones *(1)*. [b] From oxaziridine *(2d)*. [c] From the 1-pyrroline *(6)*. [d] From the hydroperoxide *(7)*. [e] B.p. = 70–82 °C/1 torr (air bath temp.). [f] In $[D_6]$DMSO.

It is proposed that the conversion *(2)*→*(4)* involves the intermediate formation of oxyl radicals *(3)* (cf. [1]). The reactions proceed to completion only when stoichiometric amounts of iron(II) sulfate are used. The reaction proceeds much more slowly when iron(II) sulfate is replaced by iron(III) chloride; furthermore, it is not catalyzed by trifluoroacetic acid. These observations support the proposed radical mechanism.

General Procedure

A solution of $FeSO_4\cdot 7H_2O$ in water is added to a solution of *(2)* in ethanol (1 : 1 molar ratio) and the resulting mixture stirred and heated under reflux for 2 h. The mixture is concentrated, the aqueous residue extracted with chloroform, and the extracts dried and concentrated to give *(4)*, which is purified by recrystallization or distillation.

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Three-Atom Ring Expansion of Cyclic Ketones *via* Nitrones and Oxaziridines

By *David St. C. Black* and *Lynn M. Johnstone*[*]

Dedicated to Professor Siegfried Hünig on the occasion of his 60th birthday

Ring-opening of bicyclic *C*-hydroxymethylene-substituted oxaziridines on treatment with iron(II) sulfate leads to *N*-(3-oxopropyl)amides[1]. This reaction can also be applied to tricyclic oxaziridines *(6)* and thus opens up a good route to a variety of eight- and nine-membered oxolactams

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