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OXIDATIVE ADDITION OF SOME *geminal* HALONITROALKANES TO IRIDIUM(I) AND PLATINUM(0) COMPOUNDS

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Summary

Oxidative addition of 1-chloro-1-nitroethane to *trans*-$IrCl(CO)[P(CH_3)_2C_6H_5]_2$ followed by treatment of the initial product with pyridine yields a new iridium(III) complex $IrCl(py)[COC(NO_2)CH_3][P(CH_3)_2C_6H_5]_2$, whose structure has been confirmed by X-ray crystallography. Two intermediate products have been observed by NMR spectroscopy; their structures have been tentatively assigned. The reaction of the corresponding bromine derivatives yields two isomers of the composition $IrBr_2(CO)[CH(NO_2)CH_3][P(CH_3)_2C_6H_5]_2$, and these are not affected by pyridine. The reaction of 1-chloro-1-nitroethane with $Pt[P(C_6H_5)_3]_4$ takes a completely different course in that it yields nitroethane and *cis*-$PtCl_2[P(C_6H_5)_3]_2$ as the main products, with no detectable formation of the products of oxidative addition. A brief mechanistic investigation points towards the participation of radicals and radical anions as transient intermediates and a mechanism is proposed which explains most of the experimental results.

Introduction

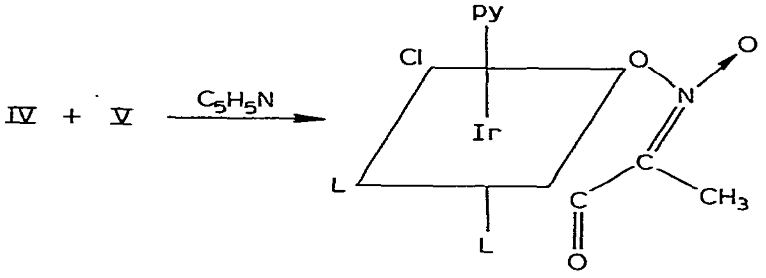
The addition reactions of covalent molecules (A—B) with low-valent transition-metal complexes have been studied extensively [1,2]. In general this reaction leads to fission of the A—B bond with a simultaneous increase in the formal oxidation state of the metal atom. Most of the information collected on the oxidative addition is based on the use of simple (monofunctional) organic addenda. We thought it of interest to explore more complex (bifunctional) addenda, with a view to preparing adducts which contain an additional reactive group which may allow subsequent transformations. This article deals mainly with the oxidative addition of 1-chloro-1-nitroethane and 1-bromo-1-nitroethane to *trans*-$IrCl(CO)[P(CH_3)_2C_6H_5]_2$ and *trans*-$IrBr(CO)[P(CH_3)_2C_6H_5]_2$, respectively.

Results

Reaction of 1-chloro-1-nitroethane with trans-IrCl(CO)[P(CH$_3$)$_2$C$_6$H$_5$]$_2$

When 1-chloro-1-nitroethane (Ia) is treated with *trans*-IrCl(CO)-[P(CH$_3$)$_2$C$_6$H$_5$]$_2$ in benzene at room temperature successive reactions take place which lead eventually to the formation of a yellow precipitate. Two unstable intermediate adducts are identified by NMR. Structures IIa and IIIa have been assigned to them; in these structures the nitroalkyl moieties are attached to the iridium atom via the oxygen atom (aci-form) and the carbon atom, respectively (see Scheme 1). After approximately 5 min, compound IIa can be observed *, and the starting materials have been consumed almost completely. Probably the phosphine ligands are mutually *cis*; all subsequent products contain *cis*-phosphine ligands, and in addition the ^{1}H NMR signals of the P—CH$_3$ groups do not appear as the expected virtual "triplet". After some 15 min product IIIa becomes observable; it is formed at the expense of product IIa. On the basis of the non-equivalence of the J(P—H) (—CH(NO$_2$)—Ir—P) couplings it can be assumed that the ligands are mutually *cis* with different *trans* ligands. Moreover, J(P—P) is small since the —P(CH$_3$)$_2$ group does not appear as a virtual "triplet". Detailed spectroscopic data of the intermediates are presented in the Experimental section. Scavenging of the intermediates with aqueous hydrochloric acid produces nitroethane as the organic product.

The formation of the final precipitated products (IV + V) is complete within about 3 h (in acetone this reaction takes only 5 min). The precipitate (IV + V) is scarcely soluble in any solvent, but it can be fractionated with chloroform into a soluble (IV) and an insoluble fraction (V). On the basis of arguments to be given later these products are assigned as indicated in Scheme 1. The only solvent which readily dissolves the precipitate is pyridine, but this also enters into reaction and after evaporation of the solvent compound VI is obtained in quantitative yield.



(VI)

Both spectroscopic and X-ray data (see Fig. 1 and Tables 1 and 2) unequivocally point to a structure consisting of an iridium(III) atom, pyridine as a ligand, mutually *cis*-phosphine ligands and the dianion of the carbonylated nitroalkyl moiety. According to NMR spectroscopy, product VI contains no

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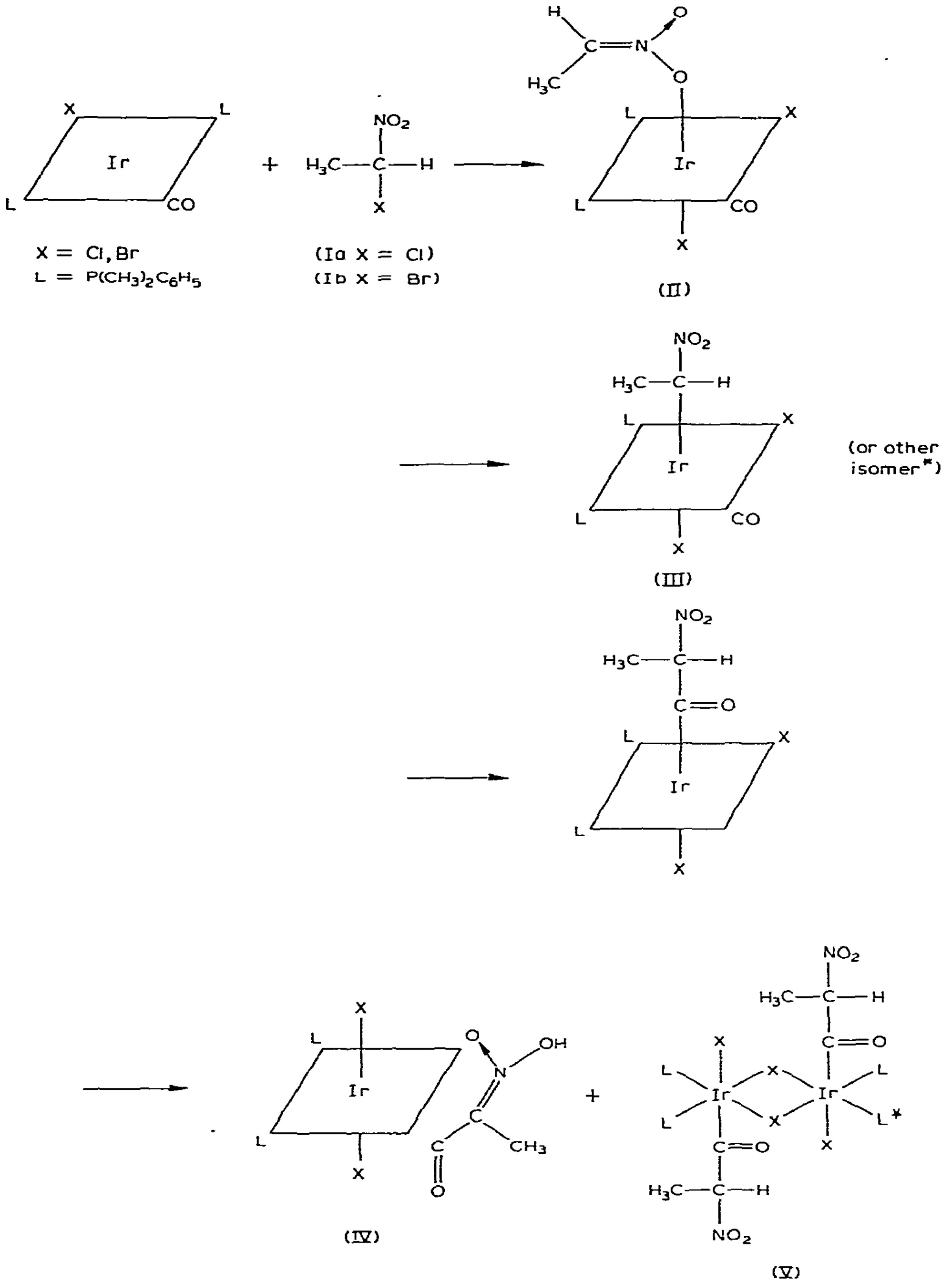
* The reaction times depend on the batch of the iridium compound used.



Scheme 1. Oxidative addition of *geminal* halo-nitroethane to Vaska's complex (L = $P(CH_3)_2C_6H_5$).

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* According to IR spectroscopy, the aci-form is equally well possible.

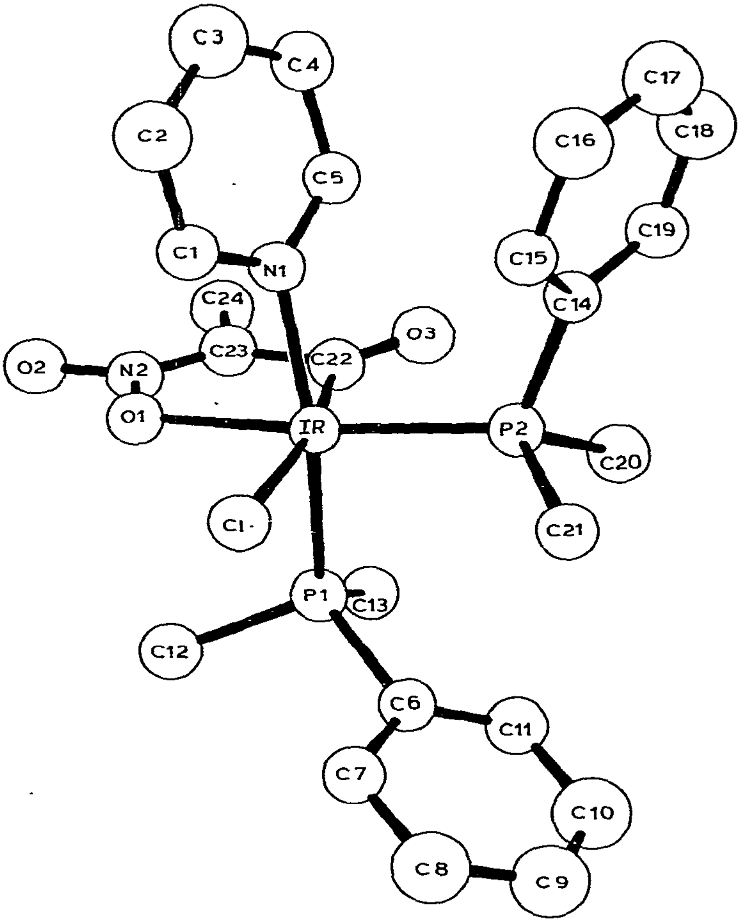


Fig. 1. Spatial representation of compound VI, the reaction product of 1-chloro-1-nitroethane, *trans*-IrCl(CO)[P(CH$_3$)$_2$C$_6$H$_5$]$_2$ and pyridine.

TABLE 1

TABLE OF SELECTED BOND DISTANCES [a] OF COMPOUND VI

Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
Ir	Cl	2.502(2)	O(1)	C(23)	2.297(9)
Ir	P(1)	2.295(2)	O(2)	N(2)	1.285(8)
Ir	P(2)	2.286(2)	O(2)	C(23)	2.296(10)
Ir	O(1)	2.087(5)	O(3)	C(22)	1.231(8)
Ir	N(1)	2.141(6)	O(4)	C(25)	1.238(13)
Ir	C(22)	1.977(7)	N(1)	C(1)	1.375(10)
P(1)	C(6)	1.808(8)	N(1)	C(5)	1.343(9)
P(1)	C(12)	1.832(9)	C(22)	C(23)	1.465(10)
P(1)	C(13)	1.823(8)	C(23)	C(24)	1.552(12)
P(2)	C(14)	1.819(8)			
P(2)	C(20)	1.824(9)			
P(2)	C(21)	1.816(8)			
O(1)	O(2)	2.224(7)			
O(1)	N(2)	1.347(8)			

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

TABLE 2

TABLE OF SELECTED BOND ANGLES [a] OF COMPOUND VI

Atom 1	Atom 2	Atom 3	Angle (°)	Atom 1	Atom 2	Atom 3	Angle (°)
Cl	Ir	P(1)	88.33(7)	Ir	O(1)	N(2)	110.2(4)
Cl	Ir	P(2)	92.78(7)	O(1)	N(2)	C(23)	119.9(6)
Cl	Ir	O(1)	88.1(1)	O(2)	N(2)	C(23)	124.7(7)
Cl	Ir	N(1)	91.0(2)	Ir	C(22)	O(3)	130.8(6)
Cl	Ir	C(22)	169.9(2)	Ir	C(22)	C(23)	110.4(5)
P(1)	Ir	P(2)	95.08(7)	O(3)	C(22)	C(23)	118.7(7)
P(1)	Ir	O(1)	88.5(1)	N(2)	C(23)	C(24)	119.4(7)
P(1)	Ir	N(1)	170.8(2)	C(22)	C(23)	C(24)	123.0(7)
P(1)	Ir	C(22)	90.9(2)				
P(2)	Ir	O(1)	176.3(1)				
P(2)	Ir	N(1)	94.1(2)				
P(2)	Ir	C(22)	97.5(2)				
O(1)	Ir	N(1)	82.3(2)				
O(1)	Ir	C(22)	81.8(3)				
N(1)	Ir	C(22)	88.2(3)				
Ir	P(1)	C(6)	118.7(3)				
Ir	P(1)	C(12)	110.4(3)				
Ir	P(1)	C(13)	116.2(3)				
C(6)	P(1)	C(12)	103.8(4)				
C(6)	P(1)	C(13)	102.6(4)				
C(12)	P(1)	C(13)	103.2(4)				
Ir	P(2)	C(14)	113.3(3)				
Ir	P(2)	C(21)	116.4(3)				
C(14)	P(2)	C(20)	103.2(4)				
C(14)	P(2)	C(21)	100.4(4)				
C(20)	P(2)	C(21)	104.7(4)				

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

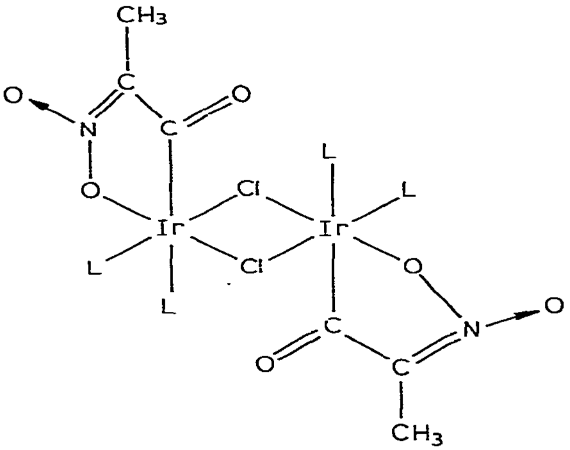
hydrides, and consists of two non-equivalent phenyl groups and four non-identical P—CH_3 groups. The ^{13}C resonance of the carbon flanked by the carbonyl and the aci-nitro function could not be observed, most probably due to its quaternary character and the nitrogen quadrupole relaxation.

The function of the pyridine is two-fold: it breaks the dimeric V into a monomer and it abstracts the acidic hydrogen adjacent to the nitro and the carbonyl group. Triphenylphosphine is also capable of monomerizing V, since V is soluble in a solution of triphenylphosphine in chloroform.

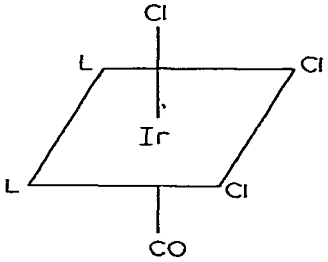
Compound VI is very stable: it resists prolonged heating (70 h at 80° C) in pyridine, irradiation with a full high-pressure mercury arc and reaction with olefins and oxygen. In pyridine-d_5 no exchange of the ligated pyridine is observed at room temperature. However, treatment with methyl iodide gives methylpyridinium iodide and a precipitate which is assigned the tentative structure VII.

Chlorination of VI with chlorine gas in chloroform gives 1,1-dichloro-1-nitroethane as the main organic product and $IrCl_3(CO)[P(CH_3)_2C_6H_5]_2$, as shown (VIII). The precursors of VI (IV and V) give the same products upon treatment with chlorine gas.

Other low-valent transition-metal complexes which are reported to be susceptible to oxidative attack [1,2] either do not give any observable reaction with 1-chloro-1-nitroethane ($IrCl[P(C_6H_5)_3]_3$, $IrCl(CO)[P(C_6H_5)_3]_2$, $Pt(C_2H_4)$-



VII



(VIII)

$[P(C_6H_5)_3]_2$, $Pd[P(C_6H_5)_3]_4$ and $RhCl[P(C_6H_5)_3]_3$) or afford nitroethane in high yield as the only organic product, without any detectable formation of the adduct ($Pt[P(C_6H_5)_3]_4$ and $Pt[P(C_6H_5)_3]_3$) *. Since all the reactions were performed in benzene, the origin of the hydrogen in the nitroethane is doubtful. $Pt[P(C_6D_5)_3]_4$ reacts with Ia in C_6D_6 in the same way as the undeuterated compound; in other words, no deuterium is incorporated into nitroethane. However, addition of D_2O to the reaction mixture causes incorporation of deuterium in the nitroethane, whereas nitroethane does not give a proton exchange in the presence of D_2O without the Pt compound present. These facts point to hydroxylic impurities as being responsible for the formation of nitroethane.

The oxidative addition of Ia to *trans*-$IrCl(CO)[P(CH_3)_2C_6H_5]_2$ seems to be exceptional, since other *geminal* chloronitroalkanes such as 1,1-dichloro-1-nitroethane and 1,1-dichloro-1-nitro-2-phenylethane, give mono-dechlorination as the main process. 2-Chloro-2-nitropropane seems to give the expected oxidative addition, but complex reactions occur subsequently.

Reaction of 1-bromo-1-nitroethane with trans-$IrBr(CO)[P(CH_3)_2C_6H_5]_2$

1-Bromo-1-nitroethane (Ib) and bromocarbonylbis(dimethylphenylphosphine)iridium(I) react in essentially the same way as the corresponding chlorine

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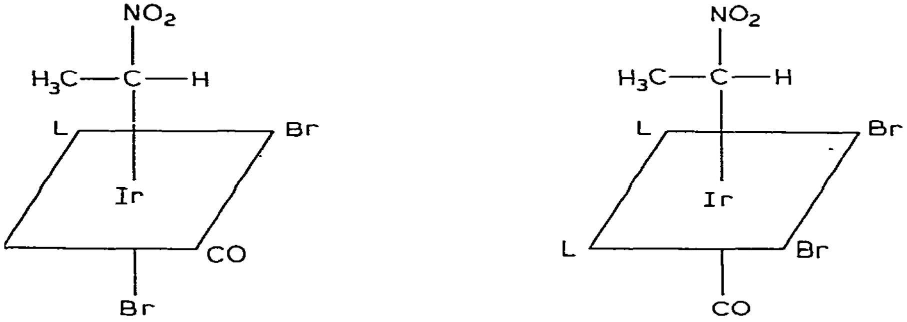
* *cis*-$PtCl_2[P(C_6H_5)_3]_2$ is produced in these reactions.

compounds do. In benzene as the solvent two isomeric compounds IIIb are formed in a ratio of 5/1. On the basis of NMR data (^1H, ^{13}C, ^{31}P) the following structures are assigned. It is not possible to decide which is the more abundant isomer.



IIb

Adduct IIb is not observed. In contrast to IIIa, the isomeric mixture IIIb is thermally stable, resists treatment with pyridine and is not susceptible to CO insertion.

Mechanism

In recent discussions at least four different mechanisms of oxidative addition have been described [3], viz. a concerted three-centered addition [4], an S_N2-type mechanism [1], a radical-pair (non-chain) mechanism [3—5,6], and, finally, a radical-chain mechanism [7,8]. Since only very slight structural changes in either the addendum or the metal compound cause the reaction to take a completely different course, and presumably proceed via a different mechanism, we have made a preliminary study of the mechanism of the reaction of 1-chloro-1-nitroethane with both *trans*-$IrCl(CO)[P(CH_3)_2C_6H_5]_2$ and $Pt[P(C_6H_5)_3]_4$.

Geminal halonitroalkanes are known to give a fast substitution of a halide ion, although a direct S_N2-type substitution has never been observed. From the work of Kornblum [9] it is evident that halide substitution occurs via radical anion intermediates. A well-known scavenger for organic radical anions is 1,4-dinitrobenzene (DNB), whose electron affinity is well above the average value for organic compounds with electron-withdrawing groups. Compound Ia reacts with *trans*-$IrCl(CO)[P(CH_3)_2C_6H_5]_2$ at 50°C to give 50% conversion within 5 min. However, in the presence of 20 mol% DNB, even after 100 min, no reaction of the addendum is observed; UV spectroscopy reveals the presence of the radical anion of DNB and its hydrolysis product, the anion of 4-nitrophenol [10]. In the absence of Ia much smaller amounts of these intermediates are formed.

2-Methyl-2-nitrosopropane is a well-known scavenger of alkyl radicals [11]. In the presence of 20 mol% of 2-methyl-2-nitrosopropane, Ia reacts with *trans*-$IrCl(CO)[P(CH_3)_2C_6H_5]_2$ at 50°C to give only 10% conversion after 5 min, even though the nitroso compound is still to a large extent in its non-reactive, dimeric form. After 105 min no further conversion is observed, and only monomeric nitroso compound is present.

Our results and recent observations [3] lead us to conclude that the reaction occurs via a radical-chain process, which must be either initiated or propagated via radical anion species, as outlined in Scheme 2.

SCHEME 2

MECHANISM OF THE REACTION OF 1-CHLORO-1-NITROETHANE WITH *trans*-$IrCl(CO)[P(CH_3)_2C_6H_5]_2$

Initiation

$$IrCl(CO)L_2 + H_3CCHCl(NO_2) \xrightarrow{SET} [IrCl(CO)L_2]^{+\cdot} + [H_3CCHCl(NO_2)]^{-\cdot} \quad (1)$$

$$[H_3CCHCl(NO_2)]^{-\cdot} \rightarrow H_3C\dot{C}H(NO_2) + Cl^- \quad (2)$$

Propagation

$$H_3C\dot{C}H(NO_2) + IrCl(CO)L_2 \xrightarrow[SET?]{via} [IrCl(CO)L_2CH(NO_2)CH_3]^\cdot \quad (3)$$

$$[IrCl(CO)L_2CH(NO_2)CH_3]^\cdot + H_3CCHCl(NO_2) \rightarrow IrCl_2(CO)L_2CH(NO_2)CH_3 + H_3C\dot{C}H(NO_2) \quad (4)$$

The first two steps (1 + 2) have their precedent in organic reaction mechanisms [9]; however, recently the single-electron transfer (SET) from a low-valent nickel complex to TCNQ (tetracyanoquinone) has been reported [12]. The two propagation steps (3 + 4) are strongly related to the propagation process in the addition of many alkyl halides to platinum(0) and palladium(0) complexes [3].

Scheme 2 only explains the effect of added inhibitors; it does not explain why the α-nitroethyl moiety is initially bound via its oxygen atom (adduct II). However, this behaviour may be expected if a single-electron transfer (SET) from the iridium compound to the α-nitroethyl radical is assumed to take place in the first propagation step [3], since in that case we have to reckon with the combination of the α-nitroethyl anion and a positively charged iridium species, which will definitely be charge controlled and lead to the aci-nitro product [13]. The α-nitroalkyl radical is highly electron deficient and consequently will easily capture an electron [14]. No explanation can be given for the difference in behaviour between the chloro and bromo compounds.

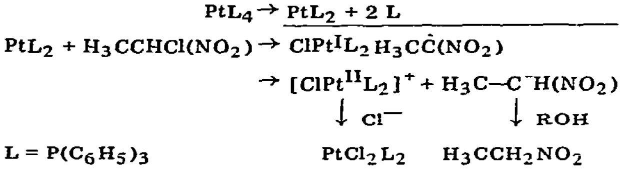
The formation of nitroethane from 1-chloro-1-nitroethane and $Pt[P(C_6H_5)_3]_4$ is inhibited neither by DNB nor by 2-methyl-2-nitrosopropane. This indicates that no chain processes via radical or radical anion intermediates are involved. It is known from literature data [3,4] that benzyl halides, for example, add to platinum(0) and some iridium(I) compounds via a radical cage process.

$$Pt^0 + RX \rightleftharpoons \overline{\dot{P}tX\ R^\cdot} \rightarrow RPtX$$

α-Nitroalkyl radicals, proposed as intermediates, are very electron deficient, and as a result tend to capture an electron to produce an α-nitrocarbanion [14]. In the presence of hydroxylic compounds this anion will react to give nitroalkane (Scheme 3).

SCHEME 3

MECHANISM OF THE REACTION OF 1-CHLORO-1-NITROETHANE WITH $Pt[P(C_6H_5)_3]_4$



Experimental

X-ray structure determination

The single-crystal X-ray study of product VI, from the reaction of Ia and *trans*-$IrCl(CO)[P(CH_3)_2C_6H_5]_2$, was carried out by Molecular Structure Corporation, P.O. Box DF, College Station, Texas 77840.

A crystal with the dimensions 0.2 × 0.2 × 0.2 mm was selected for the X-ray work. The cell was orthorombic, the space group being P_{bca}. The cell constants were obtained by computer-centering of 25 reflections, followed by least-squares refinement of the setting angle: a 28.012(3), b 12.286(2), c 14.098(1) Å, V 6036.6 Å, λ 0.71073 A, α 90, β 90, γ 90°, d(calc.) 1.63 g cm^{-3}.

Materials

trans-$IrCl(CO)[P(CH_3)_2C_6H_5]_2$ [15], *trans*-$IrBr(CO)[P(CH_3)_3C_6H_5]_2$ [15], $IrCl[P(C_6H_5)_3]_3$ [16], 2-methyl-2-nitrosopropane [17] and the *gem*-halonitroalkanes [18] were prepared according to literature procedures. $Pt[P(C_6D_5)_3]_4$ was prepared from $P(C_6D_5)_3$ using C_6D_5Br as starting material [16]. All other starting materials were either commercially available or were synthesized via standard literature procedures.

Reactions

All the reactions were carried out under argon, generally with 0.02—0.1 mmol of complex and reagent in 0.5—0.75 ml of suitable (deuterated) solvent.

Reaction of Ia with trans-$IrCl(CO)[P(CH_3)_2C_6H_5]_2$

A solution of *trans*-$IrCl(CO)[P(CH_3)_2C_6H_5]_2$ (0.097 g, 0.182 mmol) and Ia (20 μl, 0.23 mmol) in benzene (1 ml) was kept at room temperature for 3 h. The white precipitate was separated from the mother liquor by centrifugation and subsequently thoroughly washed with ether and dried in vacuo. Yield 0.044 g (0.069 mmol), 38% of compounds IV and V (calculated as $IrCl_2(COCH(NO_2)CH_3)(PMe_2Ph_2)$. The mother liquor still contained one or more iridium compounds which could not be purified or identified. The precipitate was insoluble in most common organic solvents. With chloroform the mixture could eventually be separated into a chloroform soluble (IV) and an insoluble complex (V).

Intermediate IIa. ^1H NMR (C_6D_6) with TMS as internal standard. CH_3CNO_2, $\delta = 1.49$ (d, 6 Hz); $C{-}CHNO_2$, $\delta = 5.71$ (q, 6 Hz); $P{-}CH_3$, $\delta = 1.8$ ppm and aromatic region.

Intermediate IIIa. ^{1}H NMR (C_6D_6). H_3CCNO_2, $\delta = 1.17$ (d, 7 Hz); C—$CHNO_2$, $\delta = 5.37$ (q, J(H—H) 7 Hz; d, J(P(1)—H) 5.5 Hz; d, J(P(2)—H) 8 Hz); P—CH_3, $\delta = 1.8$ ppm and aromatic region.

Product IV. ^{1}NMR ($CDCl_3$). H_3C—CNO_2, $\delta = 1.98$ (s), P—CH_3, $\delta = 1.98$ (d, 11 Hz); $\delta = 1.88$ (d, 11 Hz), $\delta = 1.49$ (d, 11 Hz), $\delta = 1.42$ ppm (d, 11 Hz) and aromatic region. IR ($CHCl_3$): 1610, 1510 and 1315 cm^{-1}.

Product V. IR (KBr): 1600, 1500, 1315 and 915 cm^{-1}.

Preparation of compound VI

A suspension of the mixture of IV and V (0.164 g, 0.26 mmol) in pyridine (5 ml) was heated at 100° C for 5 min (at room temperature a period of about 30 min was necessary). The resulting solution was filtered through glass wool. The solvent was removed in vacuo and the residue was extracted with benzene (3 X 2 ml). Evaporation of benzene in vacuo left pale yellow crystals (0.16 g, 0.22 mmol, 85%). The compound crystallized with one molecule of pyridine (next to the ligated pyridine). Crystals suitable for X-ray structure determination were obtained by recrystallization from acetone, and crystallized with one molecule of acetone. The compound was soluble in solvents such as chloroform, benzene and acetone. Anal.: Found: C, 41.2; H, 4.6; Cl, 5.1; N, 4.6. Calcd. for $C_{24}H_{30}ClIrN_2O_3P_2$: C, 42.1; H, 4.4; Cl, 5.2; N, 4.1%. ^{1}H NMR (C_5D_5N): H_3CCNO_2, $\delta = 1.93$ (s), P—CH_3, $\delta = 1.95$ (d, 11 Hz), $\delta = 1.93$ (d, 11 Hz), $\delta = 1.73$ (d, 11 Hz), $\delta = 1.41$ ppm (d, 11 Hz) and aromatic region, *o*-H of pyridine ligand at $\delta = 8.89$ ppm. ^{13}C NMR (C_5D_5N) *, H_3CCHNO_2, $\delta = 11.5$; CNO_2, not observed; P—CH_3, $\delta = 13.8$ (d, J(P—C) 45 Hz), $\delta = 13.8$ (d, 40 Hz), $\delta = 13.2$ (d, 41 Hz), $\delta = 11.2$ (d, 41 Hz), aromatic carbons; C on P, $\delta = 134.9$ ppm (d, J(C—P) 54 Hz), $\delta = 133.9$ (d, 58 Hz); *ortho*, $\delta = 132.3$ (d, J(C—P) 8.5 Hz), $\delta = 131.1$ (d, 7.4 Hz); *meta*, $\delta = 129.2$ (d, J(C—P) 11 Hz), $\delta = 128.7$ (d, 9.8 Hz); *para*, $\delta = 131.4$ (d, J(C—P) 2.5 Hz), $\delta = 130.3$ (d, 2 Hz); Ir—CO—, $\delta = 198.0$ ppm (d, 3.6 Hz; d, 6.1 Hz). ^{31}P NMR (C_5D_5N) **, $\delta = 32.7$ (d, 21 Hz), $\delta = 35.1$ ppm (d, 21 Hz). IR ($CHCl_3$), 1590, 1490, 1310 and 910 cm^{-1}.

Chlorination of IV and V

A suspension of a mixture of IV and V in chloroform was saturated with chlorine gas. The clear solution formed contained H_3C—CCl_2NO_2 (GC, NMR, IR) and *fac*-$IrCl_3(CO)[P(CH_3)_2C_6H_5]_2$ (i.e., *cis*-phosphines). ^{1}H NMR ($CDCl_3$), $\delta = 2.08$ (d, 12 Hz), $\delta = 1.72$ ppm (d, 12 Hz); ν(CO) = 2070 cm^{-1}. Anal.: Found: C, 32.9; H, 3.72; Cl, 16.83. $C_{17}H_{16}Cl_3IrOP_2$ Calcd.: C, 33.8; H, 3.65; Cl, 17.7%.

Preparation of IIIb

The mixture of isomers IIIb was prepared from Ib and *trans*-IrBr(CO)-$[P(CH_3)_2C_6H_5]_2$ in the way described for the corresponding chlorine compounds. Anal.: Found: C, 31.15; H, 3.61; Br, 22.21; N, 1.63. Calcd. for $C_{19}H_{26}Br_2IrNO_3P_2$: C, 31.2; H, 3.6; Br, 21.9; N, 1.9%. ^{1}H NMR (C_6D_6) (two isomers), H_3C—CNO_2, $\delta = 1.19$ (d, 7 Hz) and 1.33 (d, 7 Hz); H_3C—$CHNO_2$, $\delta = 5.33$ (d,

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* Internal standard TMS, C_5D_5N as the ligand.

** External standard 85% H_3PO_4.

J(P(1)—H) 5.5 Hz; d, J(P(2)—H) 8 Hz; q, J(H—H) 7 Hz), the corresponding signal of the other isomer not observed, due to overlap; P—CH_3, δ = 1.9 ppm for both isomers. ^{13}C NMR (C_6D_6), H_3C—CNO_2, δ = 20.8 and 23.3; $_3$C—CH—NO_2, δ = 56.1 (signal too small for accurate measurement of coupling) and 54.6 (d, J(C—P(1)) 3.5 Hz; d, J(C—P(2)) 2.5 Hz), the other signals are too complicated to be assigned. ^{31}P NMR (C_6D_6) * δ = 33.6 (d, 28 Hz), δ = 34.6 (d, 28 Hz) and δ = 39.4 (d, 18 Hz), δ = 39.9 ppm (d, 18 Hz). IR (C_6D_6): 2270, 2060, 1618, 1455 and 1330 cm^{-1}.

Inhibition experiments

The course of the reaction between Ia (0.1 mmol) and *trans*-IrCl(CO)-$[P(CH_3)_2C_6H_5]_2$ (0.1 mmol) in 0.75 ml of C_6D_6 was followed by NMR spectroscopy. The rate of the reaction varied with the batch and the age of the iridium complex used. Therefore the inhibition studies with DNB and 2-methyl-2-nitrosopropane (~20 mol.%) were made with all the conditions exactly the same (solvent, concentration and temperature). The rate of the uninhibited reaction as well as the extent of inhibition were then reproducible.

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* Chemical shifts given for the inner signals of the AB-pattern, since the outer peaks are very weak.