# Iridium and Platinum Complexes of Diethyl Azodicarboxylate and 4-Phenyl-1,2,4-triazoline-3,5-dione

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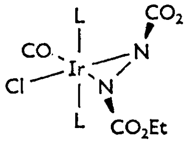
Chlorocarbonylbis(triphenylphosphine)iridium reacts in benzene with diethyl azodicarboxylate and 4-phenyl-1,2,4-triazoline-3,5-dione to form the complexes $(Ph_3P)_2Ir(NCO_2Et)_2(CO)Cl$ and $(Ph_3P)_2Ir[(NCO)_2NPh](CO)Cl$, respectively. Chlorocarbonylbis(methyldiphenylphosphine)iridium forms an analogous complex with diethyl azodicarboxylate. I.r. and $^1H$ n.m.r. studies suggest that the complexes have the phosphine ligands in a relative *trans*-configuration. Related reactions with tetrakis(triphenylphosphine)platinum gave the compounds $(Ph_3P)_2Pt(NCO_2Et)_2$ and $(Ph_3P)_2Pt[(NCO)_2NPh]$. An attempt to extend the reactions of diethyl azodicarboxylate to tetrakis(methyldiphenylphosphine)platinum and tetrakis(triphenylphosphine)palladium afforded only 1,2-bis-(ethoxycarbonyl)hydrazine. Diethyl azodicarboxylate adds to nickelocene to form a red complex, formulated as arising by addition of the azo-compound to one of the π-cyclopentadienyl rings.

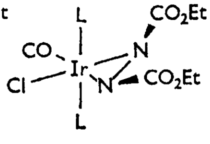
CHLOROCARBONYLBIS(TRIPHENYLPHOSPHINE)IRIDIUM undergoes a wide range of oxidative-addition reactions,[1,2] and reaction of the iridium complex with diethyl azodicarboxylate was recently reported[3] to afford the complex $(Ph_3P)_2Ir(NCO_2Et)_2(CO)Cl$, described as being too unstable for characterisation other than by i.r. spectroscopy. Herein we report our investigations of this and related systems.

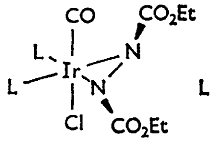
In benzene solution, diethyl azodicarboxylate reacts with chlorocarbonylbis(triphenylphosphine)iridium to form in high yield an orange-red complex (I). The i.r. spectrum shows a single terminal carbonyl band (2077s cm.$^{-1}$) in the region associated with iridium(III) carbonyl complexes, and a band at 1609s cm.$^{-1}$ assignable to an ester carbonyl group. The $^1H$ n.m.r. spectrum of (I), measured in deuteriochloroform, showed bands at τ 2·55 [30H, $C_6H_5P$], 6·30 (2H, q, $COCH_2$, $J_{HH}$ 7·0 c./sec.), 6·71 (2H, q, $COCH_2$, $J_{HH}$ 7·0 c./sec.), 8·95 (3H, t, $COCH_2CH_3$, $J_{HH}$ 7·0 c./sec.) and 9·19 [3H, t, $COCH_2CH_3$, $J_{HH}$ 7·0 c./sec.). This pattern establishes the presence of two ethoxycarbonyl groups in different chemical environments. Any one of the structures (Ia)—(Id) are consistent with these observations.

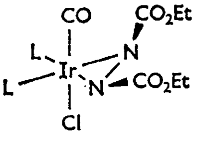
In order to limit the possibilities, chlorocarbonylbis-methyldiphenylphosphine)iridium was treated with diethyl azodicarboxylate in benzene to give $(Ph_2PMe)_2Ir(NCO_2Et)_2(CO)Cl$ (II), and the $^1H$ n.m.r. spectrum of this complex examined in deuteriochloroform. Bands occur at τ 2·5 [20H, $C_6H_5P$], 6·03 (2H, q, $COCH_2$, $J_{HH}$ 7·0 c./sec.), 6·58 (2H, q, $COCH_2$, $J_{HH}$ 7·0 c./sec.), 7·89 (6H, t, $CH_3P$, $J_{PH}$ (virtual) 4·0 c./sec.), 8·85(3H, t, $COCH_2CH_3$, $J_{HH}$ 7·0 c./sec.) and 9·06 (3H, t, $COCH_2CH_3$, $J_{HH}$ 7·0 c./sec.). The appearance of the $CH_3$–P protons as a triplet signal establishes a relative *trans*-configuration for the phosphine ligands,[4] and the spectrum is similar to that of (I) in showing the presence of two ethoxycarbonyl groups in different environments.

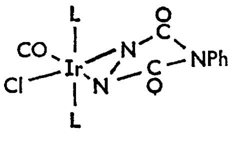
From these results it seems probable that the structures of (I) and (II) are (Ia) or (Ib), and (IIa) or (IIb) respectively, the relative configuration of the ethoxycarbonyl groups remaining undecided.

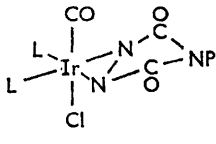

(Ia) L = $Ph_3P$
(IIa) L = $Ph_2PMe$

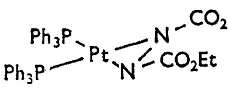

(Ib) L = $Ph_3P$
(IIb) L = $Ph_2PMe$

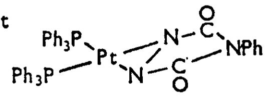

(Ic) L = $Ph_3P$
(IIc) L = $Ph_2PMe$

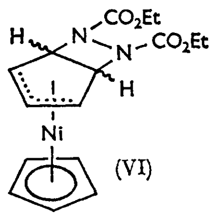

(Id) L = $Ph_3P$
(IId) L = $Ph_2PMe$

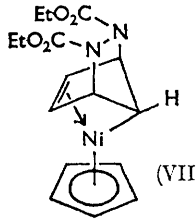

(IIIa) L = $Ph_3P$


(IIIb) L = $Ph_3P$


(IV)


(V)


(VI)


(VII)

In the spectrum of (II), in addition to the bands noted above, there were additional multiplets of low intensity indicating the presence of a small amount of an isomer of (II). The additional bands occurred at τ 2·3 (20H, $C_6H_5P$), 6·32(4H, q, $COCH_2$, $J_{HH}$ 7·0 c./sec.), 7·95 (6H, d, $CH_3P$, $J_{PH}$ 7·9 c./sec.) and 9·02 (6H, t, $COCH_2CH_3$, $J_{HH}$ 7·0 c./sec.). A structure consistent with these observations is (IId), but since attempts to

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[1] J. P. Collman, *Accounts Chem. Res.*, 1968, **1**, 136.

[2] J. P. Collman and W. R. Roper, *Adv. Organometallic Chem.*, 1968, **7**, 54.

[3] J. P. Collman and J. W. Kang, *J. Amer. Chem. Soc.*, 1967, **89**, 844.

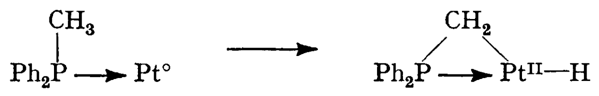
[4] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 1407.

separate this isomer were unsuccessful, this suggestion is tentative. The suggested geometry depicted in (IId) with *cis*-phosphine groups has been observed previously with the tetracyanoethylene[5] and *trans*-1,2-dicyano-1,2-bis(trifluoromethyl)ethylene[6] adducts of $(Ph_3P)_2Ir(CO)Cl$.

The question of isomerism about the N–N bond in this class of complex does not arise with the highly reactive azo-ligand 4-phenyl-1,2,4-triazoline-3,5-dione which which reacts with chlorocarbonylbis(triphenylphosphine)iridium to form the crystalline complex (III). This reaction could not be extended to $(Ph_2PMe)_2Ir(CO)Cl$, and a decision between the alternative structures (IIIa) and (IIIb) on the basis of the existence or non-existence of virtual coupling[4] in the proton n.m.r. spectrum could not therefore be made.

Tetrakis(triphenylphosphine)platinum has been found to undergo oxidative-addition reactions with a variety of molecules,[1,7] and in this manner we have prepared complexes such as $(Ph_3P)_2Pt(C_2F_4)$[8] or $(Ph_3P)_2Pt((CF_3)_2CO)$.[9] Analogous reactions occur between tetrakis(triphenylphosphine)platinum and diethyl azodicarboxylate and 4-phenyl-1,2,4-triazoline-3,5-dione to afford the crystalline complexes (IV) and (V), respectively. The $^1H$ n.m.r. spectrum of (IV) shows bands at $\tau$ 2·8 (30H, $C_6H_5P$), 6·63(4H, q, $COCH_2$, $J_{HH}$ 7·0 c./sec.) and 9·08 (6H, t, $COCH_2CH_3$, $J_{HH}$ 7·0 c./sec.), indicating that the two ethoxycarbonyl groups are in the same environment. This is consistent either with the illustrated structure, or with that of its isomer with the ester groups disposed *trans* about the N–N bond.

An attempt to prepare the complex $(Ph_2PMe)_2Pt(NCO_2Et)_2$ led to the observation of a novel hydrogenation reaction. Treatment of tetrakis(methyldiphenylphosphine)platinum with diethyl azodicarboxylate in benzene affords a deep red solution. However, work up of the reaction mixture gave only the organic compound 1,2-bis(ethoxycarbonyl)hydrazine, which must arise by a formal hydrogenation of the azo-compound. 1,2-Bis(ethoxycarbonyl)hydrazine was also formed in the reaction of tetrakis(triphenylphosphine)palladium with diethyl azodicarboxylate. When the platinum reaction was carried out in deuteriobenzene, i.r. and $^1H$ n.m.r. measurements showed, that the product $(NHCO_2Et)_2$, had not incorporated deuterium, which leads to the tentative conclusion that hydrogen transfer takes place from the co-ordinated phosphine to the azo-compound. Such a reaction could involve the oxidative tautomeric shift:



for which there are precedents in ruthenium(o)[10] and iridium(I)[11] chemistry.

The bonding in the azo-iridium and -platinum complexes is depicted as involving two bonds from the transition metal, one to each nitrogen atom. This is a convenient formalism to emphasize that the bonding is different from that in a classically $\pi$-bonded system, and signifies either of two different bonding situations: a $\sigma$-bonded rigid three-membered ring model or a system where the nitrogen atoms remain essentially $sp^2$ hybridized and the electron withdrawing substituents lower the energy of the $\pi^*$ orbitals with a resultant enhancement in back bonding from filled *d*-orbitals into the $\pi^*$ orbitals, and an increase in the rigidity of the system. Possibly there is a gradual transition, depending on the nature of the ligand, between the two limiting bonding schemes.

Nickelocene rapidly reacts with diethyl azodicarboxylate to form a crystalline 1 : 1 adduct. The $^1H$ n.m.r. spectrum measured in deuteriochloroform was of poor quality owing to decomposition in solution, however, a band was observed at $\tau$ 4·80 [5H, s, $\pi$-$C_5H_5$]. The remainder of the spectrum was poorly resolved, but showed bands in the range $\tau$ 5·95—9·16. It is suggested the reaction involves addition of the azo-compound to one of the $\pi$-cyclopentadienyl rings of nickelocene to give either (VI) (1,2-addition[12]) or (VII) (1,3-addition[13,14]).

## EXPERIMENTAL

$^1H$ n.m.r. spectra were recorded on a Varian Associates HA 100 spectrometer at 100 Mc./sec. I.r. spectra were recorded with a Perkin Elmer 257 spectrophotometer. All reactions were carried out in a nitrogen atmosphere. Light petroleum refers to the fraction having b.p. 40—60° Molecular weight measurements were made with a Mechrolab vapour-pressure osmometer using chloroform or benzene as solvent.

*Reaction Between Diethyl Azodicarboxylate and Chlorocarbonylbis(triphenylphosphine)iridium*.—Diethyl azodicarboxylate (0·5 g., 2·86 mmole) was added to a stirred solution of chlorocarbonylbis(triphenylphosphine)iridium (1·0 g., 1·28 mmole) in benzene (30 ml.). After 4 hr. at room temperature, the volume of the solvent was reduced *in vacuo* resulting in the further crystallisation of the orange-red *product* (I) (1·04 g., 85%) (Found: C, 53·9; H, 4·3; Cl, 3·6; N, 3·0; P, 6·4%; *M*, 959. $C_{43}H_{40}ClIrN_2O_5P_2$ requires C, 54·1; H, 4·2; Cl, 3·7; N, 2·9; P, 6·5%; *M*, 954), m.p. 234—235°, from methylene chloride–petroleum. $\nu_{max.}$ (Nujol or hexachlorobutadiene) 3060w, 2980w, 2930w, 2077s, 1642vw, 1609s, 1575vw, 1482m, 1438s, 1395w, 1368w, 1340w, 1307s, 1192w, 1160w, 1093m, 1072m, 760m, 712m, 698s, and 682m cm.$^{-1}$.

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[9] Beverley Clarke, M. Green, R. B. L. Osborn, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 167.

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[11] M. A. Bennett and D. L. Milner, *Chem. Comm.*, 1967, 581.

[12] D. W. McBride, R. L. Pruett, E. Pitcher, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1962, **84**, 497.

[13] D. W. McBride, E. Dudek, and F. G. A. Stone, *J. Chem. Soc.*, 1964, 1752.

[14] M. Dubeck, *J. Amer. Chem. Soc.*, 1960, **82**, 502.

*Reaction Between Diethyl Azodicarboxylate and Chlorocarbonylbis(methyldiphenylphosphine)iridium*.—Diethyl azodicarboxylate (0·5 g., 2·86 mmole) was added to a stirred solution of chlorocarbonylbis(methyldiphenylphosphine)-iridium (0·79 g., 1·20 mmole) in benzene (25 ml.). After 5 hr. at room temperature the benzene was removed *in vacuo*, and the resultant oil washed with light petroleum (5 × 20 ml.). The semicrystalline mass was recrystallised (−78°) from diethyl ether–light petroleum to give orange-yellow *crystals* of (II) (0·39 g., 40%) (Found: C, 47·9; H, 4·6; Cl, 4·5; N, 3·2; P, 7·8. $C_{33}H_{36}ClIrN_2O_5P_2$ requires C, 47·7; H, 4·4; Cl, 403; N, 3·4; P, 7·5%), m.p. 84—88°. $\nu_{max.}$ (Nujol and hexachlorobutadiene) 3060w, 2982w, 2932w, 2059s, 1690w, 1638w, 1600s, 1488m, 1470m, 1440s, 1380m, 1370m, 1345w, 1310s, 1195w, 1168w, 1100m, 1073m, 895s, 745s, and 698s cm.$^{-1}$.

*Reaction Between 4-Phenyl-1,2,4-triazoline-3,5-dione and Chlorocarbonylbis(triphenylphosphine)iridium*. A solution of 4-phenyl-1,2,4-triazoline-3,5-dione (0·23 g., 1·28 mmole) and chlorocarbonylbis(triphenylphosphine)iridium (1·0 g., 1·28 mmole) in benzene (30 ml.) was stirred at room temperature for 3 days. The volume of the dark purple solution was reduced (15 ml.) *in vacuo*. A pale yellow *solid* (III) precipitated (0·42 g., 34%) (Found: C, 55·5; H, 3·9; Cl, 3·9; P, 6·8%; *M*, 1026. $C_{45}H_{35}ClIrN_3O_3P_2$ requires C, 55·5; H, 3·7; Cl, 3·7; P, 6·5%; *M*, 955), m.p. 223–224°, from methylene chloride–light petroleum. $\nu_{max.}$ (Nujol or hexachlorobutadiene) 3058w, 2078s. 1739s, 1672s, 1655s, 1502m, 1482m, 1435s, 1285w, 1190w, 1160w, 1115w, 1090m, 1020w, 1000w, 835m, 768m, 750s, 705m, and 698s cm.$^{-1}$.

*Reaction Between Diethyl Azodicarboxylate and Tetrakis(triphenylphosphine)platinum*.—A solution of diethyl azodicarboxylate (0·80 g., 4·60 mmole) and tetrakis(triphenylphosphine)platinum (1·90 g., 1·53 mmole) in benzene (35 ml.) was set aside at room temperature for 2 days. The reaction mixture gradually became red, and after 12 hr. yellow *crystals* (0·74 g., 54%) of (IV) separated out (Found: C, 56·4; H, 4·3; N, 2·9; P, 6·9%; *M*, 860. $C_{42}H_{40}N_2O_4P_2Pt$ requires C, 56·4; H, 4·5; N, 3·1; P, 6·9%; *M*, 893], m.p. 234—235°, from methylene chloride–hexane. $\nu_{max.}$ (carbon tetrachloride) 3060w, 2980w, 2930w, 2855w, and 1640s; (Nujol) 1590w, 1575w, 1480s, 1438s, 1315s, 1275s, 1165m, 1120m, 1098s, 1070s, 1035m, 998m, 855w, 755s, 745s, 705s, 695s, and 675m cm.$^{-1}$.

*Reaction Between 4-Phenyl-1,2,4-triazoline-3,5-dione and Tetrakis(triphenylphosphine)platinum*.—A solution of 4-phenyl-1,2,4-triazoline-3,5-dione (0·997 g., 5·7 mmole) and tetrakis(triphenylphosphine)platinum (2·20 g., 1·8 mmole) in benzene (50 ml.) was stirred at room temperature for 3 days. The mixture was filtered, and benzene evaporated from the filtrate *in vacuo*. The residue was crystallised from methylene chloride–hexane to give a yellow solid, which was further purified by chromatography on a Florisil-packed column. Elution with acetone gave yellow *crystals* of (V) (0·45 g., 28%) (Found: C, 59·2; H, 4·2; P, 6·8%; *M*, 943. $C_{44}H_{35}N_3O_2P_2Pt$ requires C, 59·0; H, 4·0; P, 6·9%; *M*, 894), m.p. 191—197°. $\nu_{max.}$ (Nujol and hexachlorobutadiene) 3055w, 1730s, 1640s, 1590w, 1502m, 1490m, 1438s, 1308w, 1185w, 1115w, 1095m, 1012w, 998w, 830w, 765m, 750s, and 698s cm.$^{-1}$.

*Reaction Between Diethyl Azodicarboxylate and Tetrakis(methyldiphenylphosphine)platinum*.—A similar reaction of diethyl azodicarboxylate (0·90 g., 5·16 mmole) with tetrakis(methyldiphenylphosphine)platinum (1·72 g., 1·73 mmole in benzene (35 ml.) gave a deep red solution, after 2 days at room temperature. The solvent was removed *in vacuo* and the brown residue dissolved in methylene chloride. The supernatant liquid was decanted off, and after the volume had been reduced *in vacuo*, it was chromatographed on a Florisil-packed column. Elution with diethylether gave white crystalline 1,2-bis(ethoxycarbonyl)hydrazine (0·22 g., 25%) m.p. 128—129°, lit.[15] 131—133° (Found: C, 41·1; H, 6·7; N, 15·6; Calc. for $C_6H_{12}N_2O_4$: C, 40·9; H, 6·9; N, 15·9%). $\nu_{max.}$ (Nujol–hexachlorobutadiene) 3265s, 3040m, 2990m, 2915w, 1750s, 1690s, 1530s, 1483m, 1450m, 1440w, 1390m, 1368m, 1245s,br, 1110w, 1068m, 1020w, 900w, 798w, 785m, and 760w cm.$^{-1}$. The $^1$H n.m.r. spectrum (deuteriochloroform solution) showed bands at $\tau$ 2·03 (2H, N*H*), 5·89 (4H, q, $COCH_2$, $J_{HH}$ 7·0 c./sec.) and 8·78 (6H, t, $COCH_2CH_3$, $J_{HH}$ 7·0 c./sec.].

*Reaction Between Diethyl Azodicarboxylate and Tetrakis(triphenylphosphine)palladium*.—Diethyl azodicarboxylate (0·58 g., 3·3 mmole) was added to a stirred suspension of tetrakis(triphenylphosphine)palladium (1·1 g., 1·0 mmole) in benzene (40 ml.). After 12 hr. at room temperature, a brown solid was separated by centrifuging the reaction mixture. The solid was dissolved in methylene chloride, and addition of hexane precipitated a brown oil, which did not solidify. The supernatant liquid was separated and the solvent removed *in vacuo*. The residue was sublimed *in vacuo* to give 1,2-bis(ethoxycarbonyl)hydrazine (0·1 g., 17%) which had an i.r. spectrum identical with that of an authentic sample.

*Reaction Between Diethyl Azodicarboxylate and Nickelocene*.—Diethyl azodicarboxylate (1·85 g., 10·6 mmole) in benzene (5 ml.) was added dropwise with stirring to a solution of nickelocene (2·0 g., 10·6 mmole) in benzene (50 ml.), to give a deep red solution. After 12 hr. at room temperature, benzene was removed *in vacuo*, and the residue was dissolved in diethyl ether and filtered. Addition of hexane to the filtrate and slow evaporation *in vacuo* gave red *crystals* of (VI) or (VII) (2·90 g., 75%) m.p. 80—90° (decomp.), (Found: C, 53·1; H, 5·9; N, 8·1. $C_{16}H_{20}N_2NiO_4$ requires C, 52·9; H, 5·5; N, 7·7%). $\nu_{max.}$ (Nujol and hexachlorobutadiene) 2980m, 1710s, 1470w, 1410w, 1308m, 1252w, 1218m, 1170w, 1120w, 1055m, 1015w, 790m, and 755m cm.$^{-1}$.

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