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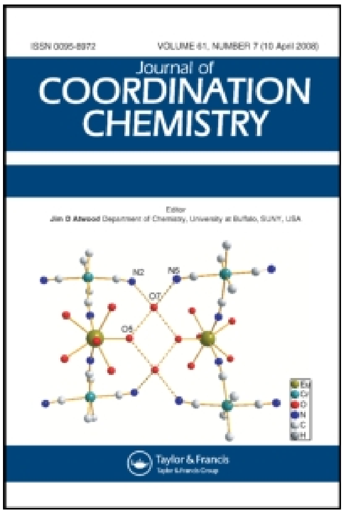

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THE PREPARATION AND CRYSTAL STRUCTURE OF BINUCLEAR μ-(α, ω-OCTA-DI-π-ENYL) NICKEL COMPOUNDS FORMED FROM BUTADIENE

T. S. Cameron[a]; M. L. H. Green[a]; H. Munakata[a]; C. K. Prout[a]; M. J. Smith[a]
[a] Chemical Crystallography and Inorganic Chemistry Laboratories, Oxford

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THE PREPARATION AND CRYSTAL STRUCTURE OF BINUCLEAR μ-(α, ω-OCTA-DI-π-ENYL) NICKEL COMPOUNDS FORMED FROM BUTADIENE

T. S. CAMERON, M. L. H. GREEN, H. MUNAKATA, C. K. PROUT and M. J. SMITH

Chemical Crystallography and Inorganic Chemistry Laboratories,
South Parks Road, Oxford OX1 3QR.

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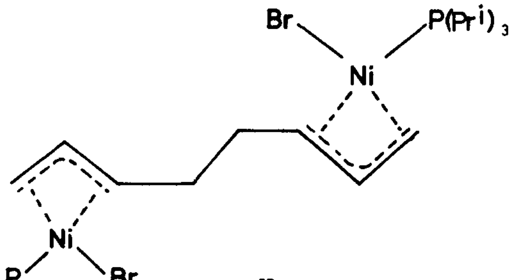
Recently we described the preparation of some moderately stable nickel methyl complexes *trans*-$(PR_3)_2NiMeBr$ (*I*, R = cyclohexyl or isopropyl).[1] We have been interested in their reaction with olefins and have found that the compound (*I*, $R = Pr^i$) reacts rapidly with butadiene. At first an intermediate green colour is formed and further reaction leads to a yellow-brown solution from which yellow-brown crystals may be isolated. The crystal structure data given below show the product to be the binuclear complex μ-(a, ω-octa-di-π-enyl)-[NiBr (PPr^i_3)]$_2$ (II).

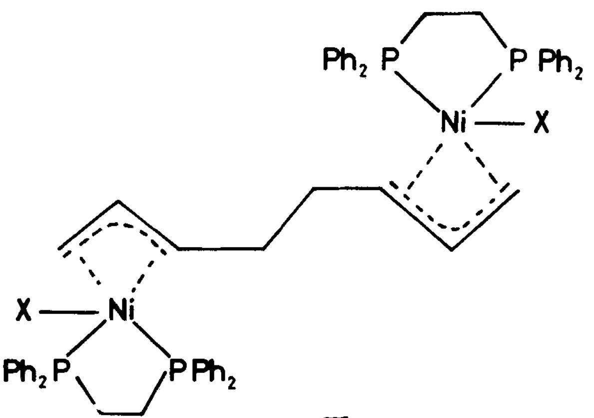


II

Treatment of the complex (II) with bis-diphenyphosphinoethane (dppe) affords an immediate reaction and a binuclear brick-red compound μ-(a, ω-octa-di-π-enyl) [NiX(dppe)]$_2$ (III, X = Br) is formed.

The crystal and molecular structures of the complexes (II) and (III, X = Br) have been determined by X-ray diffraction and the data may be briefly summarized as follows:—

Crystal data (Complex II): Triclinic, a = 13.72(1), b = 7.93(1), c = 7.89(1)Å; α = 103.1(1), β = 83.8(1), γ = 103.3(1)°. D_m = 1.435 g.cm^{-3}, D_c (for $C_{26}H_{54}Br_2Ni_2P_2$) 1.442 g.cm^{-3}. Space group P$\bar{1}$, Cu-Kα radiation, μ = 55.8cm^{-1}. 1960 independent reflections (with I>3σ), four circle diffractometer, balanced filters.



III

Crystal data (Complex III, X = Br): Monoclinic, a = 18.08(1), b = 22.18(1), c = 17.02(1)Å; γ = 110.2(1)°. D_m = 1.473 g.mc^{-3},
D_c(for 4$(C_{60}H_{61}Br_2Ni_2P_4)$.8$CHCl_3$) 1.475 g.cm^{-3}. Space group A2/a, Cu-Kα radiation, μ = 58.5 cm^{-1}, strong thermal diffuse scatter, only 1248 independent reflections (with I>3σ), four circle diffractometer, balanced filters.

Both structures were determined and refined by conventional methods. The R factors are 0.102 and 0.093 respectively.

In both crystals the complexes were found to be dimers about crystallographic symmetry centres (Figures 1 and 2), with α, ω-octa-di π-enyl bridges. However, in complex (II), C(1), C(3), P(1) and Br(1) are coplanar with the nickel atom, while in complex (III, X = Br), (C(1), (C3)), (P(1), P(2)) occupy the *cis* basal sites of a square pyramid with the bromine

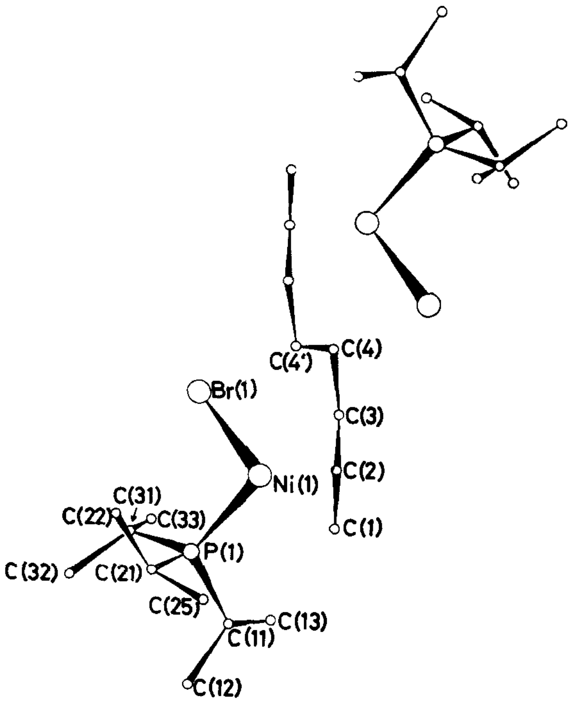


FIGURE 1. μ-(α,ω-octa-di-π-enyl)-[NiBr(PPr$_3^i$)]$_2$, complex (II). Projection through the plane perpendicular to the plane of the π-allyl groups.

atom Br(1) at the apex and the nickel atom 0.2 Å above the basal plane.

In complex (III, X = Br) the length of the nickel-bromine bond (2.66 Å) is in good agreement with the nickel-bromine bond length found in π-methallyl (bis-1, 2-(diphenylphosphino)-ethane) nickel bromide (2.671 Å)[2] and the apical bond length in $(Me_2As(CH_2)_3AsMe(CH_2)_3AsMe_2)NiBr_2$ (2.69 Å)[3]. In complex (II) the nickel bromine bond length (2.31 Å) corresponds to that of the basal Ni—Br bond in $(Me_2As(CH_2)_3AsMe(CH_2)_3AsMe_2)NiBr_2$ (2.37 Å).[3] Important bond lengths and interbond angles are summarized in the Table.

Treatment of the dppe derivative (III, X = Br) with ammonium hexafluorophosphate gives the corresponding hexaflourophosphate salt (III, $X = PF_6$). Conductivity measurements show the equivalent conductance of 10^{-3}M solutions of both salts (III, X = Br and PF_6) in nitromethane to be Λ = 51 and 92 ohm^{-1}cm^2 respectively. This suggests that the bromine is only weakly bonded to the 5-coordinated nickel, in agreement with the rather long Ni—Br bond length.

The dimerisation of the butadiene by the nickel-methyl complex gives the binuclear α, ω-octa-di-π-enyl bridging system, suggesting dimerisation by a binuclear mechanism. The mechanism is of interest since it contrasts with other mechanisms for the oligomerisation of butadiene which are thought to occur on a mononuclear nickel system by internal electron transfer.[4]

TABLE

Some interatomic distances and interbond angles

Complex I			
Ni(1)—Br(1)	2.313(3)Å	Br(1)—Ni(1)—P(1)	100.1(1)°
Ni(1)—P(1)	2.209(4)	Br(1)—Ni(1)—C(3)	91.1(4)
Ni(1)—C(1)	2.00(1)	C(3)—Ni(1)—C(1)	72.5(5)
Ni(1)—C(3)	2.11(1)	C(1)—N(1)—P(1)	96.3(5)
Ni(1)—C(2)	2.00(1)	C(1)—C(2)—C(3)	116.0(1)
Complex II			
Ni(1)—Br(1)	2.66(1)	P(1)—Ni(1)—P(2)	88.9(4)
Ni(1)—P(1)	2.19(1)	P(1)—Ni(1)—Br(1)	100.8(3)
Ni(1)—P(2)	2.18(1)	P(2)—Ni(1)—Br(1)	90.9(3)
Ni(1)—C(1)	2.07(3)	C(1)—Ni(1)—C(3)	75.0(1)
Ni(1)—C(2)	2.06(4)	C(1)—Ni(1)—P(2)	94.0(1)
Ni(1)—C(3)	2.15(3)	C(3)—Ni(1)—P(1)	99.0(1)
		C(1)—C(2)—C(3)	114.0(3)

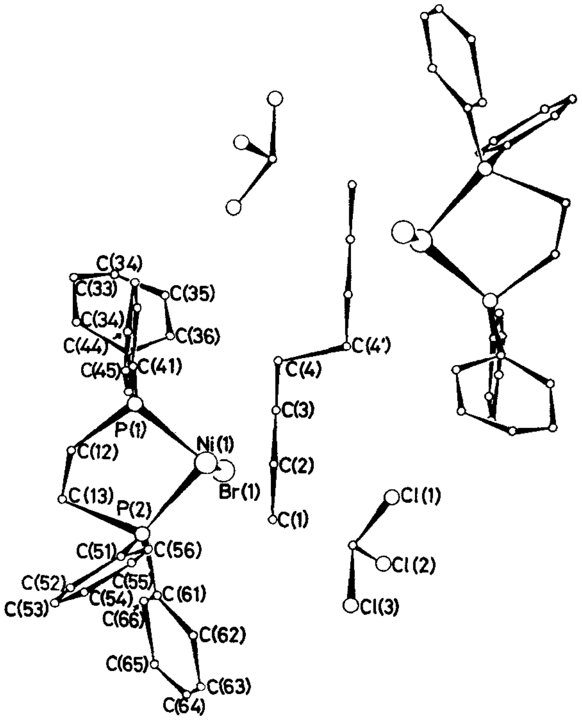


FIGURE 2. μ-(α,ω-octa-di-π-enyl)[NiX(dppe)]$_2$, complex (III, X = Br). Projection through the plane perpendicular to the plane of the π-allyl groups.

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