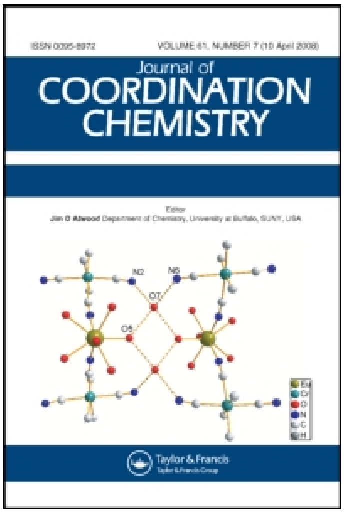

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Synthesis, Spectroscopic Characterization and X-Ray Crystal Structure of the Chloride-Bridged Face-Sharing Bioctahedral Diiridium Complex [HP-*t*-Bu$_2$Me][Ir$_2$Cl$_7$(P-*t*-Bu$_2$Me)$_2$], a Possible Precursor of the Complex [Ir(H)(Cl)$_2$(P-*t*-Bu$_2$Me)$_2$]

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SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION AND X-RAY CRYSTAL STRUCTURE OF THE CHLORIDE-BRIDGED FACE-SHARING BIOCTAHEDRAL DIIRIDIUM COMPLEX $[HP\text{-}t\text{-}Bu_2Me][Ir_2Cl_7(P\text{-}t\text{-}Bu_2Me)_2]$, A POSSIBLE PRECURSOR OF THE COMPLEX $[Ir(H)(Cl)_2(P\text{-}t\text{-}Bu_2Me)_2]$

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The reaction of an ethanolic suspension of $[NH_4]_2[IrCl_6]$ and P-*t*-Bu$_2$Me, in the presence of HCl for 15 h gives $[HP\text{-}t\text{-}Bu_2Me][Ir_2Cl_7(P\text{-}t\text{-}Bu_2Me)_2]$, **1**, in 13.5% yield. The dinuclear complex **1** was characterized by elemental analyses, IR, ^1H, ^{31}P NMR spectroscopy, and single crystal X-ray analysis. However, when the above reaction is continued for 48 h one obtains only $[Ir(H)(Cl)_2(P\text{-}t\text{-}Bu_2Me)_2]$, **2**, in good yield. It is proposed that complex **1** is a reaction intermediate to **2**. Crystallographic data for **1** (at 298 K): $a = 16.151(3)$ Å, $b = 11.885(2)$ Å, $c = 21.665(4)$ Å, $\beta = 90.26(2)°$, space group $P2_1/c (Z = 4)$.

Keywords: Crystal structure; iridium; tertiary phosphine; dinuclear complex

INTRODUCTION

We recently proposed that the dinuclear complexes $[HP\text{-}i\text{-}Pr_3][Ir_2Cl_7(P\text{-}i\text{-}Pr_3)_2]$, **3**,[1] and $[HP\text{-}i\text{-}Pr_3][Rh_2Cl_7(P\text{-}i\text{-}Pr_3)_2]$, **4**,[2] are reaction intermediates leading to the formation of $[Ir(H)(Cl)_2(P\text{-}i\text{-}Pr_3)_2]$, **5**,[1,3] and $[Rh(H)(Cl)_2(P\text{-}i\text{-}Pr_3)_2]$, **6**,[2,3] respectively. While the suggestion that the dinuclear intermediates of the type $[Ir_2Cl_7(PR_3)_2]^-$ are precursors for mononuclear complexes of the type $[Ir(H)(Cl)_2(PR_3)_2]$ (R = bulky substituent) was first proposed by Shaw[4] and coworkers, we were intrigued in comparing the crystal structure of complexes **3** and **4** with that of **1** to verify if bulky phosphines different from P-*i*-Pr_3 may influence the stereochemistry of that dinuclear compound. Here we report the synthesis and X-ray crystal structure of [HP-*t*-Bu_2Me][Ir_2Cl_7(P-*t*-Bu_2Me$)_2$], **1**.*

EXPERIMENTAL

Materials and Equipments

All starting materials and solvents, apart from P-*t*-Bu_2Me which were synthesized by literature methods,[5] were obtained commercially and used as received. The syntheses were carried out under oxygen-free nitrogen. Infrared spectra were recorded using a Perkin-Elmer 16PC Fourier-transform spectrometer. Solution ^1H and ^{31}P NMR spectra were recorded on a Bruker AMX 600.† They are referenced ^1H relative to TMS and ^{31}P relative to external H_3PO_4.

Synthesis of [HP-*t*-Bu_2Me][Ir_2Cl_7(P-*t*-Bu_2Me$)_2$], 1

Some 1 g of [$NH_4$$]_2$[$IrCl_6$] was suspended in 15 cm^3 of degassed ethanol containing 1.6 cm^3 of concentrated HCl. The suspension was refluxed for 4 h. Afterward, 2 cm^3 of P-*t*-Bu_2Me in 10 cm^3 of degassed ethanol were added. The suspension was refluxed for 15 h, then filtered. The red-brown mother liquor was left overnight. A good quantity of brown-red crystals of **1** formed. The crystals were washed with cold ethanol, ether and dried under vacuum. Yield: 0.35 g (13.5%). *Anal.* Calcd. for **1**, $C_{27}H_{64}Cl_7P_3Ir_2$ (%): C, 29.10; H, 5.80; Cl, 22.27; P, 8.34. Found:‡ C, 28.98; H, 5.77; Cl, 22.12; P, 8.16.

Synthesis of [Ir(H)(Cl$)_2$(P-*t*-Bu_2Me$)_2$], 2

Some 1 g of [$NH_4$$]_2$[$IrCl_6$] was suspended in 15 cm^3 of degassed ethanol containing 1.6 cm^3 of concentrated HCl. The suspension was refluxed for 4 h. Afterward 2 cm^3 of P-*t*-Bu_2Me in 10 cm^3 of degassed ethanol were added.

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†NMR spectra were collected at "Servizio NMR" of the Research Area of Rome.

‡Elemental analyses were made by "Servizio di Microanalisi" of Research Area of Rome.

The suspension was refluxed for 48 h, then it was filtered. The solid was washed with cold ethanol, with water ($4 \times 10\,cm^3$) to remove unreacted $[NH_4]_2[IrCl_6]$. The residue on the filter was dried in vacuum; 1.1 g of deep purple microcrystals of **2** were obtained (Yield: 81.8%). *Anal.* Calcd. for **2**, $C_{18}H_{43}Cl_2P_2Ir$ (%): C, 36.98; H, 7.43; Cl, 12.13; P, 10.59. Found: C, 36.85; H, 7.32; Cl, 11.95; P, 10.43. The IR spectrum of **2** (KBr pellets) shows a weak band at $2002\,cm^{-1}$ which is attributed to ν_{Ir-H} and in the far IR spectrum a strong band at $316\,cm^{-1}$ attributed to ν_{Ir-Cl}; these data are in agreement with those reported by Shaw and co-workers.[4] The ^1H NMR spectrum ($CDCl_3$ solution, room temperature) of **2** shows three signals: δ(P-*t*-Bu$_2$Me) = 1.48 ppm (broad signal), δ(P-*t*-Bu$_2$) = 1.38 ppm (broad signal), and δ(IrH) = −49.22 ppm (broad triplet, J(PH) = 10.5 Hz) of relative intensities 6 : 36 : 1, respectively; the above NMR data are in good agreement with those reported by Shaw and coworkers considering that they used CD_2Cl_2 solutions of **2**.[4]

X-ray Structure Solution and Refinement of [HP-*t*-Bu$_2$Me][Ir$_2$Cl$_7$(P-*t*-Bu$_2$Me)$_2$], 1

Brown-red prisms of **1** were obtained from the mother liquor. Data collection was performed by a Syntex P2$_1$ automatic diffractometer (room temperature); no decay correction was applied. The data were corrected for Lorenz and polarization effects. An empirical absorption correction, based on azimuthal scans of several reflections, was applied to intensities.[6] The structure was solved by direct methods, using programs Sir88,[7] which provided the complete structure. The latter was refined using full-matrix least-squares calculation using local programs.[8] The number of observations was 3255 ($I > 3\sigma(I)$), and the number of the variable parameter was 352 (9.25 observations for each parameter). The final R values of the observed reflections (full-matrix refinement), after introduction of the fixed contribution of 63 H atoms of the P-*t*-Bu$_2$Me groups, are $R = 0.050$ and $R_w = 0.058$. Additional details of the crystallographic experiments concerning complex **1** are given in Table I.

RESULTS AND DISCUSSION

[HP-*t*-Bu$_2$Me][Ir$_2$Cl$_7$(P-*t*-Bu$_2$Me)$_2$], 1

The IR spectrum of **1** shows a band at $2390\,cm^{-1}$ (mw) assigned to the ν_{P-H} vibration of the phosphonium cation[1,2,4] and a strong band at $324\,cm^{-1}$

TABLE I Crystal data for [HP-*t*-Bu_2Me] [Ir_2Cl_7(P-*t*-$Bu_2Me)_2$], 1

Formula	$C_{27}H_{64}Cl_7P_3Ir_2$
Mol wt	1114.37
Cryst dimens, mm	0.11 × 0.25 × 0.29
Cryst syst	monoclinic
Space group	$P2_1/c$
Cell dimens[a]	
a, Å	16.151(3)
b, Å	11.885(2)
c, Å	21.665(4)
β(°)	90.26(2)
V, Å^3	4158(1)
Z	4
Calcd density, g cm^{-3}	1.780
Scan method	$\theta/2\theta$
Radiation	MoKα ($\lambda \doteq 0.71069$ Å)
Monochromator	graphite crystal
2θ range, deg	3–48
No. of total data	11628
Variable scan speed range, deg min^{-1}	1.5–29.3
No. of obsd data, $I_o > 3\sigma(I_o)$	3255
R value for equiv reflns	0.012
μ, cm^{-1}	73.614
F(000)	2176.0
Final residuals (for 3255 data)	
R, R_w[b]	0.050 0.058
a, b, c values in the weight function $w = 1.0/(a + bF_o + F_o^2)$	65.05890 0.01472 0.00017
Goodness of fit for last cycle	0.82
Max Δ/σ for last cycle	0.04

[a] Lattice parameters calculated from 15 high-angle reflections measured at ±2θ (2θ interval 17.71–26.69°). [b] $R = \sum|F_o - F_c|/\sum|F_o|$; $R_w = \{\sum(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$.

assigned to a ν_{Ir-Cl} stretch.[1,2,4] The $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$ solution, 298 K) of **1** shows two resonances at 32.74 ppm (s) and −4.49 ppm (s) attributed to the [HP(3)-*t*-$Bu_2Me]^+$ counterion and to the two coordinated P-*t*-Bu_2Me groups, respectively (see Figure 1). The ratio of the two bands is about 1 : 2; the imperfect ratio of the two bands, as observed for the analogous rhodium dimer,[2] suggests that complex **1** is slightly dynamic in solution. ^1H NMR spectra ($CDCl_3$ solution, 298 K) show a doublet of doublets at δ(PH) = 7.22 ppm attributed to the proton of the phosphonium counterion,[1,2,4] a doublet of doublets at δ(P(3)Me) = 2.00 ppm attributed to the methyl of [HP(3)-*t*-$Bu_2Me]^+$ counterion, a doublet at δ(PMe) = 1.73 ppm attributed to the two methyl groups of the coordinated P-*t*-Bu_2Me groups, a doublet at δ(P-*t*-Bu_2) = 1.53 ppm attributed to the two *t*-Bu groups of the [HP(3)-*t*-$Bu_2Me]^+$ counterion and a doublet of doublets at δ(P-*t*-Bu_2) = 1.45 ppm attributed to the *t*-Bu groups of the two coordinated P-*t*-Bu_2Me

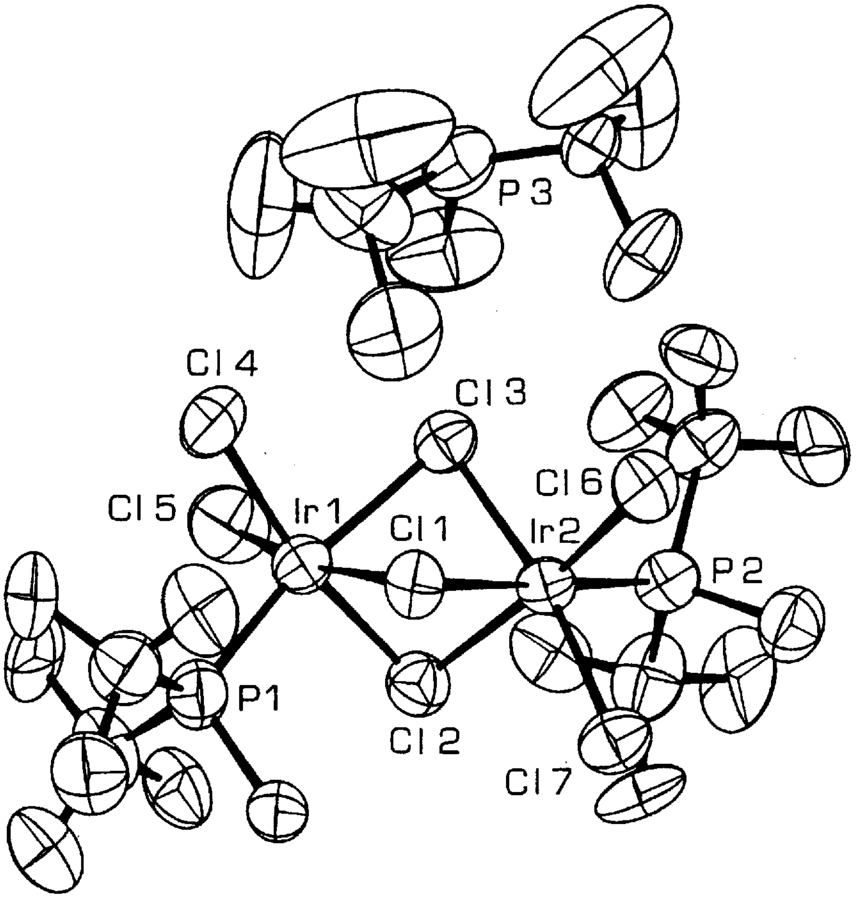

FIGURE 1 Geometry[8] of [HP-*t*-Bu_2Me][Ir_2Cl_7(P-*t*-Bu_2Me)$_2$], **1**, with hydrogen atoms of P-*t*-Bu_2Me groups omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

phosphines[1,2] (see Figure 1); the relative intensities of the mentioned bands are 1 : 3 : 6 : 18 : 36.

Molecular Structure of [HP-*t*-Bu_2Me][Ir_2Cl_7(P-*t*-Bu_2Me)$_2$], 1

Figure 1 shows perspective view of **1** and defines the atom numbering scheme for the heavy atoms. A listing of final positional parameters for non-hydrogen atoms is given in Table II. Selected bond lengths and angles are given in Tables III and IV, respectively; thermal parameters, hydrogen

TABLE II Atomic coordinates and isotropic thermal parameters, *U*eq (Å^2)*, of non-hydrogen atoms (ESDs in parentheses) for [HP-*t*-Bu_2Me][Ir_2Cl_7(P-*t*-Bu_2Me)$_2$], 1

	x/*a*	*y*/*b*	*z*/*c*	U_{eq}
Ir(1)	0.2007(1)	−0.0846(1)	−0.23027(4)	0.0689(3)
Ir(2)	0.2766(1)	0.0362(1)	−0.35186(4)	0.0604(3)
Cl(1)	0.2824(4)	0.0821(5)	−0.2398(2)	0.075(2)
Cl(2)	0.1396(3)	−0.0136(5)	−0.3220(3)	0.076(2)
Cl(3)	0.3054(3)	−0.1455(4)	−0.3120(3)	0.073(2)
Cl(4)	0.2804(4)	−0.1651(6)	−0.1526(3)	0.103(3)
Cl(5)	0.1387(4)	−0.2603(5)	−0.2440(4)	0.117(3)
Cl(6)	0.4144(3)	0.0941(5)	−0.3573(3)	0.084(2)
Cl(7)	0.2346(4)	0.2218(5)	−0.3723(3)	0.086(2)
P(1)	0.1063(4)	0.0015(5)	−0.1665(3)	0.079(2)
P(2)	0.2742(4)	−0.0100(5)	−0.4545(3)	0.075(2)
P(3)	0.5892(5)	−0.1011(5)	−0.1996(3)	0.092(3)
C(11)	0.078(2)	0.136(2)	−0.202(1)	0.10(1)
C(12)	0.145(2)	0.049(2)	−0.088(1)	0.09(1)
C(121)	0.091(2)	0.141(2)	−0.058(1)	0.13(1)
C(122)	0.149(2)	−0.050(2)	−0.042(1)	0.12(1)
C(123)	0.232(2)	0.097(2)	−0.094(1)	0.11(1)
C(13)	0.003(2)	−0.076(3)	−0.158(1)	0.10(1)
C(131)	0.015(2)	−0.191(2)	0.129(1)	0.13(1)
C(132)	−0.062(2)	−0.009(3)	−0.122(1)	0.13(1)
C(133)	−0.027(1)	−0.087(2)	−0.225(1)	0.10(1)
C(21)	0.313(2)	0.111(2)	−0.498(1)	0.10(1)
C(22)	0.169(2)	−0.034(2)	−0.488(1)	0.09(1)
C(221)	0.125(2)	−0.135(2)	−0.459(1)	0.11(1)
C(222)	0.116(2)	0.073(2)	−0.475(1)	0.12(1)
C(223)	0.167(2)	−0.052(3)	−0.557(1)	0.14(2)
C(23)	0.346(2)	−0.126(2)	−0.481(1)	0.08(1)
C(231)	0.310(2)	−0.240(2)	−0.472(1)	0.11(1)
C(232)	0.369(2)	−0.114(3)	−0.550(1)	0.12(1)
C(233)	0.429(1)	−0.124(2)	−0.445(1)	0.11(1)
C(31)	0.493(2)	−0.135(3)	−0.234(2)	0.22(3)
C(32)	0.561(3)	−0.039(3)	−0.126(2)	0.15(2)
C(321)	0.516(2)	0.075(2)	−0.137(2)	0.17(2)
C(322)	0.645(4)	−0.013(4)	−0.094(2)	0.34(5)
C(323)	0.519(4)	−0.115(4)	−0.090(2)	0.27(4)
C(33)	0.656(2)	−0.032(3)	−0.253(2)	0.14(2)
C(331)	0.624(2)	0.082(2)	−0.275(1)	0.12(1)
C(332)	0.739(2)	−0.009(5)	−0.221(4)	0.52(7)
C(333)	0.649(5)	−0.111(4)	−0.308(3)	0.41(6)

* $U_{eq} = (1/3) \sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

atomic parameters and observed and calculated structure factors are available as supplementary material, upon request, from the author.

Complex 1 is a dinuclear species, a (μ_2-Cl)$_3$-bridged, face-sharing bioctahedral compound. The distances (see Table III), both of terminal[1,2,9] and bridging[1,2,10] chloride ligands, are in the range of those reported in the literature; this does not hold for Ir(1)–Cl(3) and Ir(2)–Cl(1) of 2.559(6) Å and 2.491(5), respectively, which are longer than all others, in agreement

TABLE III Relevant bond distances (Å) for [HP-*t*-Bu$_2$Me]-[Ir$_2$Cl$_7$(P-*t*-Bu$_2$Me)$_2$], **1**, with the ESDs in parentheses; P(3)H–Cl hydrogen bond distances (Å)

Ir(1)–Cl(1)	2.390(6)	P(3)–Cl(6)[a]	3.827
Ir(1)–Cl(2)	2.370(6)	P(3)–Cl(7)[a]	3.862
Ir(1)–Cl(3)	2.559(6)		
Ir(1)–Cl(4)	2.320(7)		
Ir(1)–Cl(5)	2.334(7)		
Ir(1)–P(1)	2.302(6)		
Ir(2)–Cl(1)	2.491(5)		
Ir(2)–Cl(2)	2.381(5)		
Ir(2)–Cl(3)	2.371(5)		
Ir(2)–Cl(6)	2.334(6)		
Ir(2)–Cl(7)	2.349(6)		
Ir(2)–P(2)	2.291(6)		

[a] Symmetry code: (1 − *x*; *y* − 1/2; −*z* − 1/2).

TABLE IV Relevant bond angles (deg) for [HP-*t*-Bu$_2$Me][Ir$_2$Cl$_7$(P-*t*-Bu$_2$Me)$_2$]; ESDs are in parentheses

Cl(2)–Ir(1)–Cl(1)	80.2(2)	Cl(3)–Ir(2)–Cl(2)	81.7(2)
Cl(3)–Ir(1)–Cl(1)	78.9(2)	Cl(6)–Ir(2)–Cl(1)	87.3(2)
Cl(3)–Ir(1)–Cl(2)	78.1(2)	Cl(6)–Ir(2)–Cl(2)	167.0(2)
Cl(4)–Ir(1)–Cl(1)	95.7(2)	Cl(6)–Ir(2)–Cl(3)	95.8(2)
Cl(4)–Ir(1)–Cl(2)	169.2(2)	Cl(7)–Ir(2)–Cl(1)	89.3(2)
Cl(4)–Ir(1)–Cl(3)	91.1(2)	Cl(7)–Ir(2)–Cl(2)	91.0(2)
Cl(5)–Ir(1)–Cl(1)	165.3(2)	Cl(7)–Ir(2)–Cl(3)	168.5(2)
Cl(5)–Ir(1)–Cl(2)	92.0(2)	Cl(7)–Ir(2)–Cl(6)	89.3(2)
Cl(5)–Ir(1)–Cl(3)	86.7(2)	P(2)–Ir(2)–Cl(1)	178.3(2)
Cl(5)–Ir(1)–Cl(4)	87.7(3)	P(2)–Ir(2)–Cl(2)	101.1(2)
P(1)–Ir(1)–Cl(1)	92.9(2)	P(2)–Ir(2)–Cl(3)	97.9(2)
P(1)–Ir(1)–Cl(2)	94.1(2)	P(2)–Ir(2)–Cl(6)	91.9(2)
P(1)–Ir(1)–Cl(3)	169.3(2)	P(2)–Ir(2)–Cl(7)	92.2(2)
P(1)–Ir(1)–Cl(4)	96.6(2)	Ir(2)–Cl(1)–Ir(1)	83.3(2)
P(1)–Ir(1)–Cl(5)	100.9(3)	Ir(2)–Cl(2)–Ir(1)	86.2(2)
Cl(2)–Ir(2)–Cl(1)	79.7(2)	Ir(2)–Cl(3)–Ir(1)	82.3(2)
Cl(3)–Ir(2)–Cl(1)	80.7(2)		

with a greater *trans*-influence of P atoms than of Cl.[3,10] Also in this structure, as in the analogous species [HP-*i*-Pr$_3$][Ir$_2$Cl$_7$(P-*i*-Pr$_3$)$_2$], **3**,[1] and [HP-*i*-Pr$_3$][Rh$_2$Cl$_7$(P-*i*-Pr$_3$)$_2$], **4**,[2] is present a bifurcated hydrogen bond: P(3)–Cl(6) of 3.827 Å and P(3)–Cl(7) of 3.862 Å (see Table III); localization of the hydrogen bonded to P(3) atom was not possible. Some carbon atoms of P(3)-*t*-Bu$_2$Me show higher thermal factors; this is probably due to unresolved disorder for corresponding phosphine groups. However, these atoms could be refined without any problem.

The results indicate that the dinuclear complex [HP-*t*-Bu$_2$Me][Ir$_2$Cl$_7$(P-*t*-Bu$_2$Me)$_2$], **1**, is a likely intermediate leading to the formation of

$[Ir(H)(Cl)_2(P\text{-}t\text{-}Bu_2Me)_2]$, **2**, obtained by reacting $[NH_4][IrCl_6]$ with P-*t*-Bu_2Me in the presence of HCl; compound **2** was first obtained by Shaw and coworkers using $[H]_2[IrCl_6]$ as starting material.[4] The stereochemistry of **1**, **3**,[1] and **4**[2] is quite similar and the presence of the P-*t*-Bu_2Me phosphine in **1** instead of P-*i*-Pr_3 in **3** and **4** does not give rise to any particular modification. We are aware, as for **3**[1] and **4**,[2] that other intermediates will certainly have preceded the formation of **1**, and others will have followed it, before **2** is finally produced. However, their lifetimes were probably much shorter or/and their solubility in the reaction medium higher than **1** and **2**, thus preventing their isolation.

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Supplementary Material

Anisotropic thermal parameters, hydrogen atom positions and parameters and structure factors for complex **1** are available from the author as supplementary material, upon request.

References

[1] M. Allevi, D. Capitani, A. Ettorre and P. Mura, *Inorg. Chim. Acta*, **282**, 17 (1998), and references therein.
[2] P. Mura, *J. Coord. Chem.*, **48**, 503 (1999), and references therein.
[3] D. Capitani and P. Mura, *Inorg. Chim. Acta*, **258**, 169 (1997), and references therein.
[4] C. Masters, B.L. Shaw and R.E. Stainbank, *J. C. S. Dalton*, 664 (1972).
[5] P.C. Crofts and D.M. Parker, *J. Chem. Soc.* (*C*), 332 (1970)
[6] F. Bachechi, L. Zambonelli and G. Marcotrigiano, *J. Cryst. Mol. Struc.*, **7**, 11 (1977).
[7] M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna and D. Viterbo, *J. Appl. Cryst.*, **22**, 389 (1989).
[8] M. Camalli, D. Capitani, G. Cascarano, S. Cerrini, C. Giacovazzo and R. Spagna, SIR CAOS, Ital. Patent 35403c/86 (1986). User Guide, Istituto di Strutturistica Chimica, CNR; C.P. 10, 00016 Monterotondo Stazione, Rome, Italy.
[9] D.A. Rankin, B.R. Penfold and J.E. Fergusson, *Austr. J. Chem.*, **36**, 871 (1983) and references therein.
[10] J.A. Muir, R. Battery and M.M. Muir, *Acta Cryst.*, **B32**, 315 (1976) and references therein.