Crystal structure of *mer-trans*-iodomethyl-(3-methoxy-2-oxobenzoyl)-bis(trimethylphosphine)nickel(II), Ni[(P(CH₃)₃)₂(C₈H₆O₃)CH₃]I

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Abstract

C₁₅H₂₇INiO₃P₂, monoclinic, *P*12₁/*n*1 (no. 14), *a* = 11.3974(8) Å, *b* = 13.0518(7) Å, *c* = 13.7797(9) Å, β = 91.323(5)°, *V* = 2049.3 Å³, *Z* = 4, *R*_g(*F*) = 0.085, *wR*_{ref}(*F*²) = 0.285, *T* = 273 K.

Source of material

Onto (3-methoxy-2-oxobenzoyl)-tris(trimethylphosphine)nickel (1.00 g, 2.09 mmol) in 70 ml of ether at –70 °C was condensed CH₃I (600 mg, 4.22 mmol). The mixture was allowed to warm and was kept at 20 °C for 17 h. From the filtered solution at –27 °C orange-yellow crystals were obtained.

Experimental details

All H atoms were positioned geometrically (*d*(C–H) = 0.93–0.96 Å), and refined as riding with *U*_{iso}(H) = 1.2*U*_{eq}(carrier) or 1.5*U*_{eq}(methyl groups). The large *R* values may result from the air and temperature sensitivity of the title compound. The diffraction intensity was gradually weakened during the experiment.

Discussion

C,C-coupling reactions are effectively catalyzed by organophosphine-supported nickel(II) complexes [1]. In systems where neither spontaneous reduction to nickel(0) nor radicals are indicated, the mechanism, which usually consists of an addition/elimination reaction sequence, requires the presence of nickel(II) intermediates [2]. Klein and his co-workers reported two types of organonickel(II) compounds supported by trimethylphosphine

through oxidative addition reaction [3], but to date few organonickel(II) compounds have actually been investigated by X-ray diffraction. In this paper we reported the synthesis and the crystal structure of the title compound, which Klein had tried to synthesize [3].

In the title compound, the nickel atom is octahedrally coordinated, surrounded by two *trans* trimethyl-phosphine ligands and a meridional sequence of phenolato, acyl, methyl, and iodo ligands. The 3-methoxy-2-oxobenzoyl group acts as a bidentate ligand chelated to the nickel atom with the angle 86.7(4)°.

Table 1. Data collection and handling.

Crystal:	orange-yellow block, size 0.24 × 0.27 × 0.35 mm
Wavelength:	Mo <i>K</i> _α radiation (0.71073 Å)
μ :	26.17 cm ^{–1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{\max}$:	55.12°
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} :	10451, 4694
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ (<i>I</i> _{obs}), 2256
<i>N</i> (<i>param</i>) _{refined} :	207
Programs:	SHELXS-97 [4], SHELXL-97 [5], SHELXTL [6]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(2)	4e	0.7674	0.8173	0.1551	0.081
H(3)	4e	0.8750	0.6757	0.1696	0.100
H(4)	4e	0.7972	0.5251	0.2168	0.086
H(8A)	4e	0.3385	0.5878	0.0171	0.163
H(8B)	4e	0.4737	0.6088	0.0116	0.163
H(8C)	4e	0.3939	0.6170	–0.0823	0.163
H(9A)	4e	0.4683	0.8115	–0.1278	0.127
H(9B)	4e	0.5596	0.7996	–0.0417	0.127
H(9C)	4e	0.4801	0.8975	–0.0488	0.127
H(10A)	4e	0.2446	0.7671	–0.1206	0.174
H(10B)	4e	0.2329	0.8674	–0.0590	0.174
H(10C)	4e	0.1740	0.7656	–0.0243	0.174
H(11A)	4e	0.4333	0.6785	0.3952	0.130
H(11B)	4e	0.2958	0.6744	0.3906	0.130
H(11C)	4e	0.3605	0.7367	0.4731	0.130
H(12A)	4e	0.1613	0.8578	0.3390	0.140
H(12B)	4e	0.2304	0.9613	0.3491	0.140
H(12C)	4e	0.2231	0.8869	0.4381	0.140
H(13A)	4e	0.4653	0.9122	0.4505	0.132
H(13B)	4e	0.4672	0.9749	0.3535	0.132
H(13C)	4e	0.5486	0.8789	0.3671	0.132
H(14A)	4e	0.3325	0.9766	0.1897	0.105
H(14B)	4e	0.2260	0.9281	0.1321	0.105

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Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(14C)	4e	0.3431	0.9518	0.0789	0.105
H(15A)	4e	0.5797	0.4748	0.3734	0.148

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(15B)	4e	0.4900	0.4009	0.3213	0.148
H(15C)	4e	0.4654	0.5190	0.3237	0.148

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Ni(1)	4e	0.3698(1)	0.78862(9)	0.1722(1)	0.0373(7)	0.0412(7)	0.0584(8)	0.0005(5)	0.0108(6)	0.0001(6)
O(1)	4e	0.5588(7)	0.9260(6)	0.1505(7)	0.063(5)	0.064(5)	0.106(7)	-0.026(4)	0.014(5)	0.009(5)
O(2)	4e	0.4404(5)	0.6510(5)	0.2029(4)	0.030(3)	0.049(4)	0.052(4)	0.006(3)	0.002(3)	0.010(3)
O(3)	4e	0.5839(8)	0.4793(7)	0.2341(7)	0.080(6)	0.069(6)	0.084(6)	0.024(5)	-0.005(5)	-0.016(5)
P(1)	4e	0.3727(3)	0.7613(3)	0.0114(2)	0.061(2)	0.067(2)	0.057(2)	-0.013(2)	0.014(1)	-0.006(2)
P(2)	4e	0.3600(3)	0.8277(2)	0.3313(2)	0.064(2)	0.055(2)	0.064(2)	-0.001(1)	0.015(2)	-0.002(1)
I(1)	4e	0.16002(7)	0.69392(6)	0.17812(7)	0.0494(5)	0.0614(6)	0.1083(8)	-0.0045(3)	0.0167(4)	0.0028(4)
C(1)	4e	0.6104(9)	0.750(1)	0.1775(7)	0.040(6)	0.083(8)	0.046(6)	0.001(6)	0.009(4)	0.024(6)
C(2)	4e	0.7314(9)	0.755(1)	0.1688(8)	0.034(6)	0.11(1)	0.059(7)	0.000(6)	0.007(5)	0.028(7)
C(3)	4e	0.795(1)	0.672(1)	0.180(1)	0.041(7)	0.13(1)	0.077(9)	0.016(8)	0.022(6)	-0.006(9)
C(4)	4e	0.749(1)	0.582(1)	0.2051(9)	0.053(7)	0.10(1)	0.065(8)	0.028(7)	0.004(6)	0.001(7)
C(5)	4e	0.629(1)	0.5743(9)	0.2136(8)	0.062(7)	0.059(7)	0.060(7)	0.004(6)	0.011(6)	-0.012(6)
C(6)	4e	0.5545(9)	0.6558(8)	0.1979(7)	0.052(6)	0.057(6)	0.039(5)	0.014(5)	-0.003(5)	-0.010(5)
C(7)	4e	0.5303(9)	0.8398(9)	0.1665(8)	0.041(6)	0.063(7)	0.059(7)	-0.007(5)	-0.001(5)	-0.005(5)
C(8)	4e	0.398(2)	0.628(1)	-0.013(1)	0.16(2)	0.08(1)	0.09(1)	-0.01(1)	0.03(1)	-0.041(8)
C(9)	4e	0.483(1)	0.825(1)	-0.060(1)	0.081(9)	0.10(1)	0.077(9)	0.002(8)	0.027(7)	0.017(7)
C(10)	4e	0.241(2)	0.794(1)	-0.056(1)	0.11(1)	0.17(2)	0.068(9)	0.01(1)	0.006(9)	0.04(1)
C(11)	4e	0.363(2)	0.717(1)	0.406(1)	0.12(1)	0.078(9)	0.066(8)	0.024(8)	0.018(8)	0.015(7)
C(12)	4e	0.228(1)	0.891(1)	0.369(1)	0.14(1)	0.061(8)	0.080(9)	0.006(8)	0.045(9)	-0.009(6)
C(13)	4e	0.473(1)	0.908(1)	0.381(1)	0.09(1)	0.081(9)	0.10(1)	-0.022(8)	0.007(8)	-0.023(8)
C(14)	4e	0.310(1)	0.9297(8)	0.139(1)	0.062(7)	0.046(6)	0.102(9)	0.005(5)	0.011(7)	-0.009(6)
C(15)	4e	0.525(1)	0.468(1)	0.320(1)	0.07(1)	0.051(7)	0.17(2)	-0.010(7)	0.01(1)	0.005(9)

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