Heterotetranuclear $M_2(d^0)M'_2(d^8)$ (M = Ti or Zr, M′ = Rh or Ir) Complexes containing Pyridine-3,5-dicarboxylate as an Assembling Ligand. Crystal Structure of $[(\eta^5\text{-}C_5H_5)_2Ti\{\mu\text{-}3,5\text{-}C_5H_3N(CO_2)_2\}_2Ti(\eta^5\text{-}C_5H_5)_2]$†

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Reaction of $[M(\eta^5\text{-}C_5H_5)_2Cl_2]$ (M = Ti, **1a** or Zr, **1b**) in tetrahydrofuran (thf) with pyridine-3,5-dicarboxylic acid, in the presence of NEt_3, gives the homobinuclear species $[(\eta^5\text{-}C_5H_5)_2M\{\mu\text{-}3,5\text{-}C_5H_3N(CO_2)_2\}_2M(\eta^5\text{-}C_5H_5)_2]$ (M = Ti, **2a** or Zr, **2b**) in good yields. The crystal structure of the titanium derivative **2a** has been determined by X-ray analysis. The compound crystallizes in the monoclinic space group $P2_1/c$, with $a = 12.666(4)$, $b = 7.914(3)$, $c = 16.443(7)$ Å, $\beta = 108.21(3)°$ and $Z = 2$; $R = 0.053$ and $R' = 0.086$. The molecule consists of two $(\eta^5\text{-}C_5H_5)_2Ti$ units linked by two pyridine-3,5-dicarboxylato ligands. Only one oxygen atom of each carboxylato group is involved in bonding to the titanium atoms, giving a 16-membered ring. The two pyridine rings are almost coplanar and adopt an orientation with the nitrogen atoms at the exterior of the ring. The geometry around the titanium atoms is nearly tetrahedral. Complexes **2a** and **2b** contain unco-ordinated pyridine nitrogen atoms which have been utilised in the synthesis of heterotetranuclear complexes. Reaction of **2a** or **2b** with $[\{Rh(CO)_2Cl\}_2]$ or $[Ir(CO)_2(p\text{-}MeC_6H_4NH_2)Cl]$ in dichloromethane gives complexes $[(\eta^5\text{-}C_5H_5)_2M\{\mu\text{-}3,5\text{-}C_5H_3N(CO_2)_2M'(CO)_2Cl\}_2M(\eta^5\text{-}C_5H_5)_2]$ (M = Ti, M′ = Rh, **3a**; M = Zr, M′ = Rh, **3b**; M = Ti, M′ = Ir, **4a**; M = Zr, M′ = Ir, **4b**) in near quantitative yields. Spectroscopic data support a structure in which the $M'(CO)_2Cl$ moieties are bonded to the pyridine nitrogen atoms in complexes **2a** and **2b**. These are the first reported examples of complexes containing pyridine-3,5-dicarboxylate as an assembling ligand.

Heterobimetallic complexes containing both early electron-deficient and late electron-rich transition metals are of current interest for their potential importance in catalysis[1] and organic synthesis.[2] In principle such complexes are able to promote activation of a substrate molecule by utilising both metals; the early electron-deficient metals are oxophilic agents and can act as Lewis acids[3] while the late electron-rich metals could display oxidative addition, reductive elimination and insertion reactions.[4] Additional interest in such systems also arises because they can be useful models for the phenomenon of 'strong metal-support interactions' observed in heterogeneous catalysis for catalysts in which late transition metals are deposited on supports of an early transition metal.[5]

Convenient synthetic routes to heterobinuclear species containing both early and transition metals have been described recently.[3,6,7] Stephan[6] developed synthetic routes in which a functionalized early transition-metal complex acts as a metal-containing ligand to bind to a later transition metal. We have extended this synthetic route to prepare complexes containing d^0 (Ti^{IV} and Zr^{IV}) and d^8 (Rh^I and Ir^I) metal centres held together by pyridine-3,5-dicarboxylato ligands. Here we report the results obtained together with the X-ray crystal and molecular structure of the homobinuclear species $[(\eta^5\text{-}C_5H_5)_2Ti\{\mu\text{-}3,5\text{-}C_5H_3N(CO_2)_2\}_2Ti(\eta^5\text{-}C_5H_5)_2]$.

Results and Discussion

The titanium(IV) and zirconium(IV) pyridine-3,5-dicarboxylato bridged bimetallic complexes $[(\eta^5\text{-}C_5H_5)_2M\{\mu\text{-}3,5\text{-}C_5H_3N(CO_2)_2\}_2M(\eta^5\text{-}C_5H_5)_2]$ (M = Ti, **2a** or Zr, **2b**) were prepared by treating $[M(\eta^5\text{-}C_5H_5)_2Cl_2]$ (M = Ti, **1a** or Zr, **1b**) with pyridine-3,5-dicarboxylic acid in the presence of NEt_3 in tetrahydrofuran (thf) at room temperature. The reaction proceeds in a similar manner for both **1a** and **1b** and leads to the almost quantitative formation of the corresponding complexes **2a** and **2b**, which are isolated as yellow, crystalline air-stable solids. They are almost insoluble in all the common organic solvents; the insolubility in methanol allows their separation from $NHEt_3Cl$. Compounds **2a** and **2b** have not been characterized completely by spectroscopy; fast atom bombardment (FAB) mass spectral experiments failed to give significant information owing to the insolubility of the complexes but their dimeric nature was established by the X-ray crystal-structure determination of **2a**.

The ^1H NMR spectra of **2a** and **2b** in $CDCl_3$ solution, show singlet resonances for the cyclopentadienyl protons. The reactions of **1a** and **1b** with pyridine-2,6-dicarboxylic acid in the presence of NEt_3, in varying molar ratio, have been reported;[8] the reaction products are the complexes $[M(\eta^5\text{-}C_5H_5)_2\{2,6\text{-}C_5H_3NCO_2(CO_2H)\}Cl]$ and $[M(\eta^5\text{-}C_5H_5)_2\{2,6\text{-}C_5H_3NCO_2(CO_2H)\}_2]$ (M = Ti or Zr) in which one carboxylate group is chelated to the metal centre while the hydroxyl proton of the other carboxylic groups is retained. Starting from $[TiMe_2(\eta^5\text{-}C_5H_5)_2]$ the reaction with pyridine-2,6-dicarboxylic acid yields the five-co-ordinate derivative $[Ti(\eta^5\text{-}C_5H_5)_2\{2,6\text{-}C_5H_3N(CO_2)_2\}]$, containing two carboxyl oxygen atoms and the pyridine nitrogen atom co-ordinated to the metal.[9] The reaction of **1a** with pyridine-2,6-dicarboxylic acid in the presence of NEt_3 gave mainly insoluble products which were probably polymeric species and could not be characterized; only small quantities of $[Ti(\eta^5\text{-}C_5H_5)_2\{2,6\text{-}C_5H_3N(CO_2)_2\}]$ were formed in the re-

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† Bis(μ-pyridine-3,5-dicarboxylato-κO^3:κO^5)-bis[bis(η^5-cyclopentadienyl)titanium(IV)].

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Selected bond lengths (Å) and angles (°) for complex **2a**

Ti–O(1)	1.961(3)	Ti–C(8)	2.350(8)
Ti–C(9)	2.377(7)	Ti–C(10)	2.377(9)
Ti–C(11)	2.357(7)	Ti–C(12)	2.346(8)
Ti–C(13)	2.336(5)	Ti–C(14)	2.376(7)
Ti–C(15)	2.375(6)	Ti–C(16)	2.326(13)
Ti–C(17)	2.344(6)	O(2)–C(1)	1.221(5)
O(1)–C(1)	1.293(5)	O(3)–Ti′	1.958(3)
O(3)–C(7)	1.282(7)	C(1)–C(2)	1.487(5)
O(4)–C(7)	1.223(7)	C(2)–C(6)	1.384(7)
C(2)–C(3)	1.383(6)	C(4)–C(5)	1.370(8)
C(3)–C(4)	1.375(5)	C(5)–N(1)	1.338(7)
C(4)–C(7)	1.505(6)	C(8)–C(9)	1.360(9)
N(1)–C(6)	1.330(6)	C(9)–C(10)	1.339(12)
Ti • • • Ti′	7.736(1)		
Cp′(1)–Ti–Cp′(2)	132.7(2)	C(7)–O(3)–Ti′	135.7(3)
O(3′)–Ti–Cp′(2)	106.5(2)	O(1)–C(1)–C(2)	115.2(3)
O(3′)–Ti–Cp′(1)	106.2(2)	C(4)–C(5)–N(1)	123.7(5)
O(1)–Ti–Cp′(2)	106.6(2)	C(2)–C(6)–N(1)	123.2(4)
O(1)–Ti–Cp′(1)	105.3(2)	O(3)–C(7)–C(4)	114.8(4)
O(1)–Ti–O(3′)	92.4(1)	C(5)–N(1)–C(6)	117.1(5)
Ti–O(1)–C(1)	134.3(2)	O(3)–C(7)–O(4)	125.1(5)
O(1)–C(1)–O(2)	124.6(3)	O(4)–C(7)–C(4)	120.1(5)
O(2)–C(1)–C(2)	120.2(4)		

Table 2 Atomic coordinates (× 10^4) for **2a**

Atom	*z*	*y*	*z*
Ti	2988(1)	1799(1)	775(1)
O(1)	2207(2)	159(3)	−100(2)
O(2)	3460(2)	−1012(5)	−620(2)
O(3)	−1634(2)	−2353(4)	−1052(2)
O(4)	−2055(3)	−4131(7)	−2154(3)
C(1)	2510(3)	−873(5)	−595(2)
C(2)	1604(3)	−1928(5)	−1161(2)
C(3)	549(3)	−2028(5)	−1084(2)
C(4)	−224(3)	−3042(5)	−1646(3)
C(5)	89(4)	−3949(8)	−2243(4)
N(1)	1100(3)	−3857(7)	−2335(3)
C(6)	1838(3)	−2858(6)	−1796(3)
C(7)	−1399(3)	−3231(7)	−1628(4)
C(8)	4173(5)	3250(8)	164(5)
C(9)	3214(7)	2996(8)	−486(4)
C(10)	2403(6)	3877(10)	−318(7)
C(11)	2792(8)	4697(8)	430(8)
C(12)	3926(7)	4347(9)	752(5)
C(13)	4110(7)	1595(9)	2201(3)
C(14)	3298(4)	425(9)	2114(4)
C(15)	3429(8)	−740(7)	1580(5)
C(16)	4322(10)	−272(19)	1329(4)
C(17)	4728(4)	1098(18)	—1740(6)

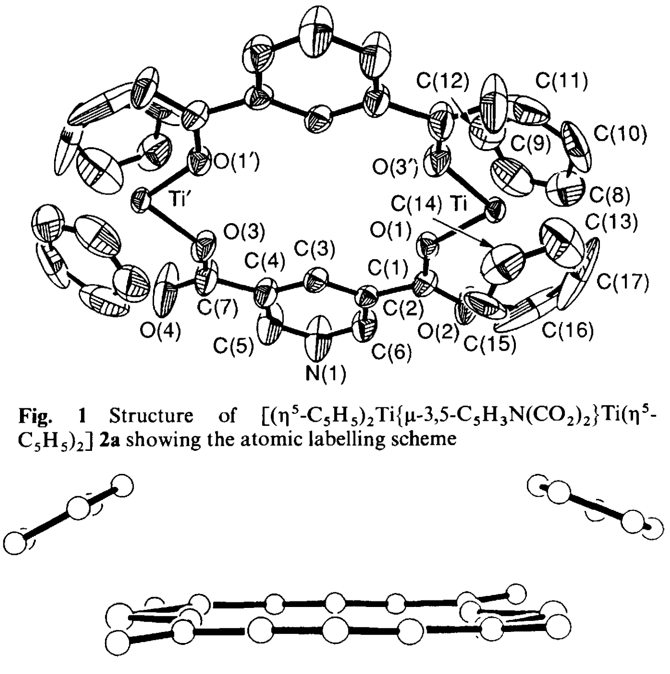


Fig. 1 Structure of $[(\eta^5\text{-}C_5H_5)_2Ti\{\mu\text{-}3,5\text{-}C_5H_3N(CO_2)_2\}Ti(\eta^5\text{-}C_5H_5)_2]$ **2a** showing the atomic labelling scheme

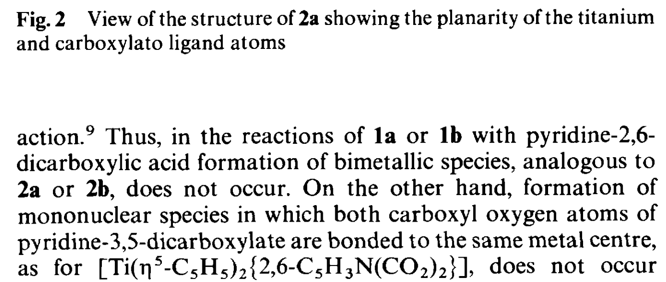
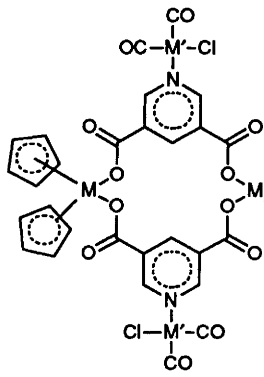


Fig. 2 View of the structure of **2a** showing the planarity of the titanium and carboxylato ligand atoms

action.[9] Thus, in the reactions of **1a** or **1b** with pyridine-2,6-dicarboxylic acid formation of bimetallic species, analogous to **2a** or **2b**, does not occur. On the other hand, formation of mononuclear species in which both carboxyl oxygen atoms of pyridine-3,5-dicarboxylate are bonded to the same metal centre, as for $[Ti(\eta^5\text{-}C_5H_5)_2\{2,6\text{-}C_5H_3N(CO_2)_2\}]$, does not occur owing to steric hindrance arising from interaction of the *para* hydrogen of the pyridine ring with the metal centre.

The crystal structure of **2a** consists of discrete dimeric centrosymmetric molecules with no unusual intermolecular contacts. Figs. 1 and 2 show two views of **2a** with the atom-labelling scheme. Selected bond lengths and angles are given in Table 1 and fractional atomic coordinates in Table 2. The molecule consists of two $(\eta^5\text{-}C_5H_5)_2Ti$ units linked by two pyridine-3,5-dicarboxylato ligands. Only one oxygen atom of each carboxylato group is involved in bonding to the titanium atoms, giving a 16-membered ring; the Ti–O(1) and Ti′–O(3) bond distances of 1.961(3) and 1.958(3) Å respectively are nearly identical. The two pyridine rings are almost coplanar and adopt an orientation with the nitrogen atoms lying at the exterior of the ring. The geometry around the titanium atoms is distorted tetrahedral with the Cp′(1)–Ti–Cp′(2) angle of 132.7(2)° [Cp′(1) and Cp′(2) are the centroids of the C(8)–C(12) and C(13)–C(17) cyclopentadienyl rings respectively] being greater than that formed by other ligands. The pyridine-3,5-dicarboxylato ligands have normal structural parameters;[10] the Ti–C bond lengths are in the range normally found for bis(cyclopentadienyl)titanium complexes.[9,10]

Complexes **2a** and **2b** contain unco-ordinated pyridine nitrogen atoms which should be suitable for the synthesis of new types of heterometallic complexes containing both early electron-deficient and late electron-rich transition metals. The reaction of **2a** or **2b** with $[\{Rh(CO)_2Cl\}_2]$ at room temperature, in dichloromethane solution, gives the tetranuclear complexes $[(\eta^5\text{-}C_5H_5)_2M\{\mu\text{-}3,5\text{-}C_5H_3N(CO_2)_2Rh(CO)_2Cl\}_2M(\eta^5\text{-}C_5H_5)_2]$ (M = Ti, **3a** or Zr, **3b**) in near quantitative yields. For the synthesis of the analogous iridium(I) complexes, the readily available starting material $[Ir(CO)_2(p\text{-}MeC_6H_4NH_2)Cl]$ was used; this reacts with **2a** or **2b** analogously to the rhodium precursor to generate the corresponding iridium complexes **4a** (M = Ti) and **4b** (M = Zr). The tetranuclear complexes **3a**,**3b** and **4a**,**4b** are yellow, air-stable solids, almost insoluble in thf and chlorinated solvents and completely insoluble in common organic solvents. Taking into account the molecular structure of the precursors **2a** and **2b**, complexes **3a**,**3b** and **4a**,**4b** were considered to be tetranuclear species; FAB mass spectra however did not give satisfactory information owing to the insolubility of the complexes. However analytical and spectroscopic data are in accord with the formulation proposed. The IR spectra (Nujol mulls) show two terminal ν(CO) bands at frequencies which compare very well with those of $[Rh(CO)_2(py)Cl]$ (py = pyridine)[11] and $[Ir(CO)_2(p\text{-}MeC_6H_4NH_2)Cl]$;[12] the persistence of the cyclopentadienyl ring bands and of the co-ordinated pyridine-3,5-dicarboxylate indicates that the basic structure of the precursors **2a** and **2b** is



	M	M′
3a	Ti	Rh
3b	Zr	Rh
4a	Ti	Ir
4b	Zr	Ir

retained. The ^{1}H NMR spectra of **4a** and **4b** in $CDCl_3$ solution are in agreement with the proposed structure; the cyclopentadienyl proton resonance are singlets at chemical shifts very similar to those of the precursors. Complexes **3a** and **3b** were more insoluble than the corresponding Ir complexes so preventing the recording of reliable NMR spectra.

Complexes **3a**, **3b**, **4a** and **4b** appear to show no reactivity toward small molecules probably owing to their insolubility.

Experimental

All reagents were purchased and used as supplied. Solvents were dried by standard procedures. All experiments were performed under an atmosphere of purified nitrogen. Infrared spectra were obtained on Nujol mulls by using a Perkin-Elmer FT IR 1720 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker WP80-SY spectrometer, operating at 80.13 MHz. Elemental analyses were performed by Malissa-Reuter Mikroanalytisches Laboratorium, Elbach, Germany and by the Microanalytical Laboratory of the Organic Chemistry Institute of Milan.

Preparations.—$[(\eta^5\text{-}C_5H_5)_2Ti\{\mu\text{-}3,5\text{-}C_5H_3N(CO_2)_2\}_2Ti(\eta^5\text{-}C_5H_5)_2]$ **2a**. A thf solution of NEt_3 (0.121 g, 1.2 mmol) was added, with stirring, to a suspension containing $[Ti(\eta^5\text{-}C_5H_5)_2Cl_2]$ (0.15 g, 0.6 mmol) and pyridine-3,5-dicarboxylic acid (0.10 g, 0.6 mmol). The mixture was stirred for 2 h at room temperature during which time an orange solid was formed while the supernatant became colourless. The solid was filtered off and washed several times with methanol to remove the $NHEt_3Cl$ and then dried *in vacuo* (0.19 g; 0.57 mmol, 95%). IR (KBr, Nujol): $\nu(CO_2)$ 1630 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 6.68 (s, 10 H, C_5H_5), 8.51 (t, 1 H, C_5H_3N) and 9.4 (d, 2 H, C_5H_3N) (Found: C, 59.45; H, 3.85; N, 4.10. Calc. for $C_{17}H_{13}NO_4Ti$: C, 59.50; H, 3.80; N, 4.10%).

$[(\eta^5\text{-}C_5H_5)_2Zr\{\mu\text{-}3,5\text{-}C_5H_3N(CO_2)_2\}_2Zr(\eta^5\text{-}C_5H_5)_2]$ **2b**. In a similar manner to the preparation of **2a** above, the compound was synthesized in 95% yield by the reaction of $[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$ (0.178 g, 0.6 mmol) with pyridine-3,5-dicarboxylic acid (0.100 g, 0.6 mmol) in the presence of NEt_3 (0.121 g, 1.2 mmol) in thf and a reaction time of 1 h. The compound was isolated as a white solid. IR (KBr, Nujol) $\nu(CO_2)$ 1636 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 6.39 (s, 10 H, C_5H_5), 9.5 (m, 3 H, C_5H_3N) (Found: C, 52.50; H, 3.45; N, 3.50. Calc. for $C_{17}H_{13}NO_4Zr$: C, 52.85; H, 3.40; N, 3.60%).

$[(\eta^5\text{-}C_5H_5)_2Ti\{\mu\text{-}3,5\text{-}C_5H_3N(CO_2)_2Rh(CO)_2Cl\}_2Ti(\eta^5\text{-}C_5H_5)_2]$ **3a**. Solid **2a** (0.144 g, 0.21 mmol) was added, with stirring, to a solution of $[\{Rh(CO)_2Cl\}_2]$ (0.085 g, 0.22 mmol) in $CHCl_3$ (40 cm^3). A red-orange solid was rapidly formed from the resulting suspension. After 15 min, it was filtered off, washed with $CHCl_3$ and dried *in vacuo* (0.216 g, 0.201 mmol, 96%). IR (KBr, Nujol) $\nu(CO)$ 2002 and 2073, $\nu(CO_2)$ 1640 cm^{-1} (Found: C, 42.60; H, 2.45; Cl, 6.60; N, 2.60. Calc. for $C_{19}H_{13}ClNO_6RhTi$; C, 42.45; H, 2.45; Cl, 6.60; N, 2.60%).

$[(\eta^5\text{-}C_5H_5)_2Zr\{\mu\text{-}3,5\text{-}C_5H_3N(CO_2)_2Rh(CO)_2Cl\}_2Zr(\eta^5\text{-}C_5H_5)_2]$ **3b**, $[(\eta^5\text{-}C_5H_5)_2Ti\{\mu\text{-}3,5\text{-}C_5H_3N(CO_2)_2Ir(CO)_2Cl\}_2Ti(\eta^5\text{-}C_5H_5)_2]$ **4a** *and* $[(\eta^5\text{-}C_5H_5)_2Zr\{\mu\text{-}3,5\text{-}C_5H_3N(CO_2)_2Ir(CO)_2Cl\}_2Zr(\eta^5\text{-}C_5H_5)_2]$ **4b**. These compounds were synthesized in a similar manner to **3a**. Compound **3b** was obtained as a pale yellow solid, in 97% yield, from **2b** (0.100 g, 0.129 mmol) and $[\{Rh(CO)_2Cl\}_2]$ (0.050 g, 0.13 mmol) in $CHCl_3$ and a reaction time of about 3 h. IR (KBr, Nujol) $\nu(CO)$ 2087 and 2010, $\nu(CO_2)$ 1657 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 6.38 (s, 10 H, C_5H_5), 9.48 (m, br, 3 H, C_5H_3N) (Found: C, 39.10; H, 2.35; Cl, 6.20; N, 2.35. Calc. for $C_{19}H_{13}ClNO_6RhZr$: C, 39.30; H, 2.25; Cl, 6.10; N, 2.40%).

Compound **4a** was obtained as orange solid, in 98% yield, from **2a** (0.157 g, 0.229 mmol) and $[Ir(CO)_2(p\text{-}MeC_6H_4NH_2)Cl]$ (0.172 g, 0.459 mmol) in $CHCl_3$ and a reaction time of 15 min. IR (KBr, Nujol) $\nu(CO)$ 2062 and 1983, $\nu(CO_2)$ 1645 cm^{-1} (Found: C, 36.20; H, 2.15; Cl, 5.55; N, 2.40. Calc. for $C_{19}H_{13}ClIrNO_6Ti$: C, 36.40; H, 2.10; Cl, 5.65; N, 2.25%).

Compound **4b** was obtained as a beige solid, in 96% yield, from **2b** (0.108 g, 0.139 mmol) and $[Ir(CO)_2(p\text{-}MeC_6H_4NH_2)Cl]$ (0.105 g, 0.279 mmol) in $CHCl_3$ and a reaction time of 2 h. IR (KBr, Nujol) $\nu(CO)$ 2076 and 1994, $\nu(CO_2)$ 1661 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 6.40 (s, 10 H, C_5H_5), 9.52 (m, br, 3 H, C_5H_3N) (Found: C, 33.90; H, 2.05; Cl, 5.20; N, 2.10. Calc. for $C_{19}H_{13}ClIrNO_6Zr$: C, 34.05; H, 1.95; Cl, 5.30; N, 2.10%).

X-Ray Data Collection and Structure Refinement.—Suitable crystals of **2a** were obtained by slow evaporation of a CH_2Cl_2 solution. Diffraction measurements were made on a Siemens R3m/v four-circle diffractometer using graphite-monochromated Mo-Kα (λ = 0.710 73 Å) radiation. Accurate unit-cell dimensions and crystal orientation matrices were obtained from least-squares refinement of 2θ, ω, χ and ψ values of 25 strong reflections in the range $14 < 2\theta < 28°$. The compound crystallizes in the monoclinic space group $P2_1/c$, with a = 12.666(4), b = 7.914(3), c = 16.443(7) Å, β = 108.21(3)°, U = 1565.6(10) Å^3, Z = 2, D_c = 1.456 g cm^{-3}, μ(Mo-Kα) = 5.57 cm^{-1} and $F(000)$ = 704. Lorentz and polarization corrections were applied to the intensity data but no absorption correction was made owing to the low absorption coefficient and the fairly uniform dimensions of the crystal. The structure was solved by using direct methods, successive least-squares refinements and difference Fourier maps. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were added at calculated positions and included in the structure factor calculations with a common thermal parameter (U = 0.08 Å^2 for H atoms of pyridine ring and U = 0.12 Å^2 for the others). Scattering factors for non-hydrogen atoms were taken from ref. 13 and for hydrogen atoms from ref. 14. Anomalous dispersion correction for Ti was taken from ref. 15. Of 3431 measured independent reflections 2237 having $I > 3\sigma(I)$ were used to refine 208 parameters to final residuals of R 0.053 and R' 0.086, $w = 1.00/[\sigma^2(F_o) + 0.0043F_o^2]$, quality-of-fit indicator = 1.21, largest peak = 0.79 e Å^{-3} near the carbon atoms of the cyclopentadienyl rings.

All calculations were performed with the SHELX 76[16] and PARST[17] set of programs on the IBM 4341 computer at the Centro di Calcolo dell' università di Messina.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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