Transition Metal Complexes with Terminal or Bridging Imidato(1 −) Ligands. *X*-Ray Crystal Structures of *trans*-$[Ir(CO)(\overline{NCOC_2F_4CO})(PPh_3)_2]$ and $[\{Pd(o\text{-}C_6H_4CH{=}NPh)(\mu\text{-}\overline{NCOC_2H_4CO})\}_2]\cdot CH_2Cl_2$,† Spectroscopic Studies of $[Mn(CO)_5(\overline{NCOC_2H_4CO})]$, and the Nature of the Metal–Nitrogen Bond

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The reaction of $[Mn(CO)_5Br]$ with the thallium(I) salt of succinimide yields the novel succinimidato(1 −) complex $[Mn(CO)_5(\overline{NCOC_2H_4CO})]$. The imide-derived ligand is found to behave as a pseudo-halogen in terms of its σ-acceptor and π-donor properties by 'Graham' analysis of i.r. spectroscopic data. Mononuclear arylpalladium complexes, *trans*-$[Pd(Ph)(im)(PPh_3)_2]$ [im = imidato(1 −) ligand], and related carbonyl–rhodium and –iridium complexes, *trans*-$[M(CO)(im)(PPh_3)_2]$, may be synthesised by reaction of the corresponding chloro-complexes with succinimide, phthalimide, or tetrafluorosuccinimide. The structure of *trans*-$[Ir(CO)(\overline{NCOC_2F_4CO})(PPh_3)_2]$ has been established crystallographically (Ir–N 2.09 Å). Binuclear arylpalladium complexes containing halide or acetate bridges react with imides in the presence of base to give complexes in which the imidato(1 −) ligand adopts a novel bridging co-ordination mode, *via* nitrogen and one of the carbonyl oxygens. The structure of one complex of this type, $[\{Pd(o\text{-}C_6H_4CH{=}NPh)(\mu\text{-}\overline{NCOC_2H_4CO})\}_2]\cdot CH_2Cl_2$, has been confirmed crystallographically.

During a study of possible new catalytic routes to aromatic amines it became evident to us that, although many transition metal (M) complexes containing imidato(1 −) ligands, $(RCO)_2N^-$, derived typically from phthalimide or succinimide, have been synthesised,[1–5] and some even structurally characterised[6,7] as containing unidentate N-bonded ligands, relatively little was known of the electronic nature of the M–N bond in such complexes. It has however been shown by Graham[8] that an estimate of the σ- and π-donor/acceptor properties of a ligand, X, may be obtained by analysis of the carbonyl stretching frequencies of its pentacarbonylmanganese derivative $[Mn(CO)_5X]$, and we have therefore prepared the succinimidato(1 −) complex $[Mn(CO)_5(\overline{NCOC_2H_4CO})]$ for this purpose. In addition, a new series of arylpalladium and carbonyl–rhodium and –iridium complexes containing imidato(1 −) ligands have been prepared as potential reagents for the synthesis of N-arylimides.

Results and Discussion

The pale yellow crystalline complex $[Mn(CO)_5(\overline{NCOC_2H_4CO})]$ (1) was obtained in modest yield by reaction of the thallium(I) salt of succinimide with $[Mn(CO)_5Br]$ in dichloromethane at room temperature. The i.r. spectrum of complex (1) (cyclohexane solution, ±0.1 cm^{-1}) showed strong bands in the carbonyl region at 2 136.1 (A_1), 2 052.0 (E), 1 999.2 (A_1), and 1 652.5 cm^{-1} (imidato carbonyl, Table 1), together with very weak ^{13}CO bands at 2 075.8 (B_1, ^{13}CO), 2 021.4 (E, ^{13}CO), and 1 956.1 cm^{-1} (A_1, ^{13}CO). The metal–carbonyl stretching [ν(CO)] force constants (N m^{-1} × 10^2) were calculated using the Cotton–Kraihanzel approximation[9] to be 16.130 (k_1), 17.490 (k_2), and 0.245 (k_i) respectively. Analysis of these force constants by the method of Graham[8] (in which the succinimide-derived ligand is regarded as neutral) yielded σ- and π-parameters of +1.32 (strong σ-acceptor) and −0.65 (moderate π-donor), so that the 'neutral' succinimido ligand closely resembles a halogen. For comparison, the values[8] for chlorine are +1.25 (σ) and −0.57 (π), whereas the phenyl ligand has σ = +0.18 (weak σ-acceptor) and π = −0.03 (weak π-donor), and triphenylsilyl, a ligand of completely opposite type to halogen, has σ = −0.55 (strong σ-donor) and π = +0.40 (moderate π-acceptor). Thus, despite mesomeric withdrawal of 'lone-pair' π-electron density from nitrogen by the two imidato-carbonyl groups, the ligating atom clearly retains a substantial degree of the π-donor character normally associated with a filled *p* orbital on nitrogen. Since we are dealing with a filled-shell (18-electron) complex, it is clear that nitrogen π-donor character will give rise to significant p_π–d_π *repulsions* in the M–N bond, which should in turn enhance delocalisation of the nitrogen lone pair onto the imidato-carbonyl groups. This effect, combined with the known σ-donor properties of transition metal centres,[10] immediately accounts for the very low imidato-carbonyl stretching frequency of 1 652 cm^{-1} [$\nu_{asym}(C{=}O)$] observed for the imidato(1 −) ligand in $[Mn(CO)_5(\overline{NCOC_2H_4CO})]$ (*cf.* 1 708 cm^{-1} for

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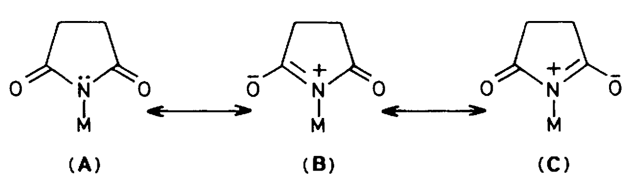
† *trans*-Carbonyl(tetrafluorosuccinimidato-*N*)bis(triphenylphosphine)iridium and 1,2-bis[*o*-(phenyliminomethyl)phenyl-C^1,*N*]-di-μ-[succinimidato-*O*(Pd^1),*N*(Pd^2); *O*′(Pd^2),*N*′(Pd^1)]dipalladium—dichloromethane (1/1) respectively.

Supplementary data available (No. SUP 56510, 8 pp.): thermal parameters, full bond lengths and angles for **(6c)**, least-squares planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii–xx. Structure factors are available from the editorial office.

Table 1. Infrared and ^{1}H n.m.r. spectroscopic data

Complex	I.r. (ν/cm^{-1})[a]	^{1}H N.m.r. (δ/p.p.m.)[b]
(1)	2 136.1w [ν(CO), A_1], 2 052.0s [ν(CO), E], 1 999.2s [ν(CO), A_1], 1 652.5m [ν(CO), imide]	2.76 (s, 4 H, $-C_2H_4-$)
(2a)	1 605s [ν(CO)]	7.1—7.6 (m, 30 H, PPh_3), 6.2—6.7 (m, 5 H, Pd–Ph), 1.38 (s, 4 H, $-C_2H_4-$)
(2b)	1 640s [ν(CO)]	7.0—7.6 (m, 34 H, PPh_3 + $-C_6H_4-$), 6.1—6.6 (m, 5 H, Pd–Ph)
(2c)	1 673s [ν(CO)]	7.0—7.6 (m, 30 H, PPh_3), 6.2—6.8 (m, 5 H, Pd–Ph)
(3a)	1 615s [ν(CO)]	7.48—7.89 (m, 20 H, PPh_2), 6.77—7.20 (m, 5 H, Pd–Ph), 2.18—2.45 (m, 4 H, PC_2H_4P), 2.21 (s, 4 H, OCC_2H_4CO)
(3b)	1 620s [ν(CO)]	6.5—8.0 (m, 29 H, aromatic), 1.9—2.6 (m, 4 H, PC_2H_4P)
(4)	1 682s [ν(CO)]	6.9—8.2 (m, 20 H, PPh_2), 1.8—3.0 (m, 4 H, PC_2H_4P)
(5a)	1 980s [ν(CO), RhCO], 1 620s [ν(CO), imide]	7.2—8.0 (m, 30 H, PPh_3), 1.28 (s, 4 H, $-C_2H_4-$)
(5b)	1 990s [ν(CO), RhCO], 1 640s [ν(CO), imide]	6.6—8.0 (m, 34 H, aromatic)
(5c)	1 995s [ν(CO),RhCO], 1 679s [ν(CO), imide]	7.3—7.9 (m, 30 H, PPh_3)
(6a)	1 975s [ν(CO), IrCO], 1 630 [ν(CO), imide]	7.2—7.9 (m, 30 H, PPh_3), 1.25 (s, 4 H, $-C_2H_4-$)
(6b)	1 958s [ν(CO), IrCO], 1 650, 1 630s [ν(CO), imide]	6.8—7.9 (m, 34 H, aromatic)
(6c)	1 981s [ν(CO), IrCO], 1 686s [ν(CO), imide]	
(7a)	1 720m [ν_{sym}(CO)], 1 610s [ν_{asym}(CO)]	*c*
(7b)	1 780m [ν_{sym}(CO)], 1 660s [ν_{asym}(CO)]	7.25 (s, 2 H), 6.84 (dd, 2 H), 6.67—6.83 (m, 8 H), 6.43 (td, 2 H), 6.24 (dd, 4 H), 5.49 (dd, 2 H)
(7c)	1 720s [ν_{sym}(CO)], 1 590s [ν_{asym}(CO)]	6.4—7.2 (m, 8 H, $-C_6H_4-$), 3.34 (q, 4 H, $-CH_2-N$), 2.88 (s, 6 H, NCH_3), 2.68 (s, 8 H, $-C_2H_4-$), 1.96 (s, 6 H, NCH_3)

[a] Obtained on KBr pellets. [b] $CDCl_3$ Solution. [c] See Figure 4.



Scheme 1. Canonical forms of the succinimidato(1 –) ligand

$Et-\overline{NCOC_2H_4CO}$ [11]), since canonical forms involving C–O single bonds [Scheme 1, (**B**) and (**C**)] now make significant contributions to the structure of the ligand.

This proposal directly contradicts a previous explanation of the low imidato-carbonyl stretching frequencies observed in many transition metal derivatives. It has been suggested [1,2] that, in certain Pd^{II} and Pt^{II} complexes, electron release *from* the imidato-carbonyl groups *via* nitrogen to the metal could account for the low ν(C=O) frequencies, but since π-electron-withdrawing N-substituents are in fact known to *raise* these frequencies [*e.g.* $PhSO_2\overline{NCOC_2H_4CO}$ [12] shows ν_{asym}(C=O) at 1 740 cm^{-1}], the combined effects of M $\longrightarrow$ N σ-donation and π–π repulsions in the M–N bond seem to provide a much more reasonable explanation.

The halogen-like character of the succinimido ligand suggested to us that, since certain palladium and rhodium complexes promote carbon–halogen bond formation (*e.g.* in the decarbonylation of aroyl halides [13]) the formation of carbon–nitrogen bonds might prove possible by arylation of pre-formed palladium- or rhodium-imidato(1 –) complexes, or by reductive elimination of N-arylimides from complexes containing both aryl and imidato(1 –) ligands. This type of approach did not in fact lead to the discovery of new C–N bond-forming reactions,* but a series of novel imidato(1 –) complexes was isolated in the course of our work and are described below.

The phenylpalladium complexes *trans*-[PdCl(Ph)(PPh_3)$_2$] [14] and *cis*-[PdCl(Ph)(dppe)] (dppe = $Ph_2PCH_2CH_2PPh_2$) reacted readily with succinimide or phthalimide in CH_2Cl_2 at room temperature, in the presence of triethylamine, to give the corresponding imidato(1 –) complexes (**2a**), (**2b**) and (**3a**), (**3b**) respectively (Table 2). Tetrafluorosuccinimide [15] behaved anomalously, however, reacting with the *trans* complex in the usual way to give (**2c**), but with the *cis* complex to cleave the phenyl–palladium bond and yield the chloro-tetrafluorosuccinimidato(1 –) complex (**4**). This result implies that the greater acidity of tetrafluorosuccinimide may in fact allow oxidative addition of the N–H bond to palladium(II), followed by reductive elimination of benzene from a transient Pd^{IV} intermediate. Oxidative addition of imide N–H bonds to Pd^0 and Pt^0 is of course well established, but the previously described [1] isolation of a bis[succinimidato(1 –)] complex from the reaction of [Pd(PPh_3)$_4$] with succinimide can again perhaps be most readily rationalised in terms of a *double* oxidative addition (Pd^0 $\longrightarrow$ Pd^{II} $\longrightarrow$ Pd^{IV}) followed by elimination of H_2 from a Pd^{IV} intermediate.

Our attempts to promote reductive elimination of N-phenylimides from the Pd^{II} complexes (**2**) and (**3**) by thermolysis in dimethyl sulphoxide in the presence of excess triphenylphosphine or 1,2-bis(diphenylphosphino)ethane (dppe) indeed gave high yields of the corresponding zerovalent palladium complexes [Pd(PPh_3)$_4$] and [Pd(dppe)$_2$], but the imidato(1 –) ligand was invariably recovered after work-up only as free, unsubstituted, imide. The known [16] reductive elimination of quaternary phosphonium ions from Pd^{II} may provide the mechanism for reduction in this case.

The rhodium(I) and iridium(I) complexes *trans*-[M(CO)(PPh_3)$_2$Cl] also reacted with imides, in the presence of a tertiary amine, to substitute chloride and yield the imidato(1 –) complexes (**5**) and (**6**) respectively (Table 2). Reaction of complex (**5a**) with iodobenzene at 160 °C (refluxing mesitylene) resulted in loss of the imidato(1 –) ligand and yielded *trans*-[Rh(CO)(PPh_3)$_2$I]. The fate of the imidato(1 –) ligand in this reaction is unclear, although formation of N-phenylsuccinimide can certainly be ruled out on the basis of t.l.c. analysis of the product mixture.

The structure of the tetrafluorosuccinimidato(1 –) iridium complex (**6c**) was confirmed crystallographically, and is shown in Figure 1. Selected bond lengths and angles are displayed in Table 3. The plane of the imidato(1 –) ligand is rotated some 72° from the co-ordination plane of the metal, and there is a slight tetrahedral distortion of the geometry about iridium such that the angle P–Ir–P is reduced from 180° to 172°, and the angle

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* However, a phthalimidato(1 –)nickel(II) complex has been reported to yield *N*-phenylphthalimide on reaction with bromobenzene.[4]

Table 2. Analytical data (%) (calculated values in parentheses)

Complex	C	H	N
(**1**) $[Mn(CO)_5(\overline{NCOC_2H_4CO})]$	36.8 (36.9)	1.3 (1.4)	4.7 (4.8)
(**2a**) *trans*-$[Pd(Ph)(\overline{NCOC_2H_4CO})(PPh_3)_2]$	67.9 (68.5)	5.0 (4.9)	1.5 (1.7)
(**2b**) *trans*-$[Pd(Ph)(\overline{NCOC_6H_4CO})(PPh_3)_2]$	69.9 (70.3)	4.6 (4.6)	1.4 (1.6)
(**2c**) *trans*-$[Pd(Ph)(\overline{NCOC_2F_4CO})(PPh_3)_2]$	63.0 (62.9)	4.3 (4.0)	1.5 (1.6)
(**3a**) *cis*-$[Pd(Ph)(\overline{NCOC_2H_4CO})(Ph_2PCH_2CH_2PPh_2)]\cdot CHCl_3$	55.4 (55.6)	4.4 (4.3)	1.7 (1.7)
(**3b**) *cis*-$[Pd(Ph)(\overline{NCOC_6H_4CO})(Ph_2PCH_2CH_2PPh_2)]$	65.4 (66.0)	4.6 (4.6)	1.8 (1.9)
(**4**) *cis*-$[PdCl(\overline{NCOC_2F_4CO})(Ph_2PCH_2CH_2PPh_2)]$	50.5 (50.7)	3.7 (3.4)	1.9 (2.0)
(**5a**) *trans*-$[Rh(CO)(\overline{NCOC_2H_4CO})(PPh_3)_2]$	65.0 (65.3)	4.6 (4.6)	1.7 (1.9)
(**5b**) *trans*-$[Rh(CO)(\overline{NCOC_6H_4CO})(PPh_3)_2]$	67.5 (67.4)	4.6 (4.3)	2.0 (1.8)
(**5c**) *trans*-$[Rh(CO)(\overline{NCOC_2F_4CO})(PPh_3)_2]$	59.4 (59.7)	3.7 (3.7)	1.7 (1.7)
(**6a**) *trans*-$[Ir(CO)(\overline{NCOC_2H_4CO})(PPh_3)_2]$	58.1 (58.4)	4.4 (4.1)	1.8 (1.7)
(**6b**) *trans*-$[Ir(CO)(\overline{NCOC_6H_4CO})(PPh_3)_2]$	61.1 (60.7)	4.0 (3.9)	2.0 (1.6)
(**6c**) *trans*-$[Ir(CO)(\overline{NCOC_2F_4CO})(PPh_3)_2]$	53.9 (53.8)	3.5 (3.3)	1.4 (1.5)
(**7a**) $[\{Pd(C_6H_4CH{=}NPh)(\mu\text{-}\overline{NCOC_2H_4CO})\}_2]\cdot CH_2Cl_2$	49.0 (49.2)	3.7 (3.5)	6.4 (6.6)
(**7b**) $[\{Pd(C_6H_4CH{=}NPh)(\mu\text{-}\overline{NCOC_2F_4CO})\}_2]\cdot CH_2Cl_2$	42.4 (42.1)	2.8 (2.2)	5.6 (5.6)
(**7c**) $[\{Pd(C_6H_4CH_2NMe_2)(\mu\text{-}\overline{NCOC_2H_4CO})\}_2]$	46.4 (46.1)	4.6 (4.8)	8.4 (8.3)

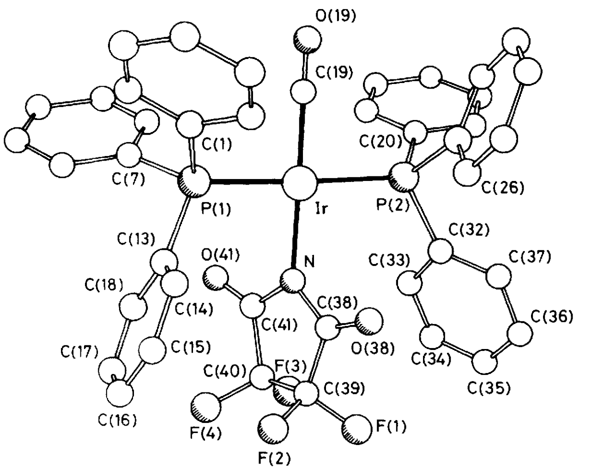
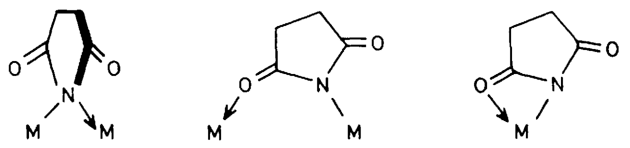


Figure 1. The structure of $[Ir(CO)(\overline{NCOC_2F_4CO})(PPh_3)_2]$ (**6c**)

N–Ir–C(19) to 177°. The Ir–N bond length of 2.087(4) Å may be compared to a value[17] of 2.133(8) Å in the pyridine complex $[Ir(C_5H_5N)(CO)_2Cl]$.

The imidato(1 –) ligand adopts an apparently sterically congested position between two phenyl rings (Figure 1), with a number of atom–atom contacts approaching, or even less than, the sum of van der Waals radii. These include: N–C(33) 3.18, O(38)–C(32) 3.24, C(41)–C(18) 3.18, O(41)–C(18) 3.28, and N–C(13) 3.27 Å. It seems curious that the preferred conformation of the two eclipsed triphenylphosphines leaves the relatively small carbonyl ligand in a sterically open position while the tetrafluorosuccinimidato(1 –) ligand is so crowded, but this may simply reflect the well known tendency of aromatic systems to form 'stacked' structures in the solid state, as a result of either charge transfer or (as possibly in this case) the cumulative effect of *attractive* van der Waals interactions.

The binuclear, *ortho*-metallated palladium complexes $[\{Pd(o\text{-}C_6H_4CH_2NMe_2)Cl\}_2]$[18] and $[\{Pd(o\text{-}C_6H_4CH{=}NPh)(O_2CMe)\}_2]$[19] reacted with succinimide and tetrafluorosuccinimide, to give an entirely novel type of complex (**7**) (Table 2) in which the imidato(1 –) ligand replaces a *bridging* halide or acetate group. Two bridging structures are conceivable for the imidato(1 –) ligand, involving either a tetrahedral bridging nitrogen atom or an N–C–O bridging unit resembling the O–C–O fragment of a bridging acetate ligand (Scheme 2). A third possibility is that the imidato(1 –) ligand could behave in *chelate* fashion giving mononuclear products, as has been proposed[5] though not yet confirmed, for $[RuH(PPh_3)_3(\overline{NCOC_2H_4CO})]$.



Scheme 2. Alternative modes of bidentate co-ordination for the succinimidato(1 –) ligand

Unlike the other imidato(1-) complexes, (**7a**)—(**7c**) showed two strong i.r. bands in the imidato-carbonyl region (1 500—1 800 cm^{-1}). The higher frequency mode [ν_{sym}(CO)] is normally very weak in cyclic imides and indeed, in the spectra of compounds (**1**)—(**6**), has negligible intensity compared with the antisymmetric ν(CO) absorption. Co-ordination of one carbonyl group to the metal however, as in the NCO-bridging and -chelating structures, would remove the two-fold symmetry of the imidato(1-) ligand and thereby increase the intensity of the ν_{sym}(CO) absorption.

The symmetrical N-bridging structure and the chelating structure were in fact ruled out immediately by the ^1H n.m.r. spectrum of the succinimidato(1 –) complex (**7c**). The benzylic methylene group appears as an AB quartet (δ 3.34 p.p.m., J_{AB} = 14 Hz) and the N-methyl groups are clearly in different environments, appearing as singlets at δ 1.96 and 2.88 p.p.m. In the essentially planar structure required by a chelating imidato(1 –) ligand the methylene and methyl protons would each be equivalent, giving rise only to a pair of singlets of relative intensity 1:3. The symmetrical N-bridged structure would also produce this type of spectrum, since the benzylic ligands would be constrained to coplanarity both with each other and with the palladium atoms. Thus, only the possibility of an asymmetric –NCO– bridging mode remains, and by analogy with certain acetate-bridged complexes,[20,21] this might

Table 3. Selected bond lengths and angles for $[Ir(CO)(NCOC_2F_4CO)(PPh_3)_2]$ (**6c**), with estimated standard deviations in parentheses

Bond lengths (Å)

Ir–P(1)	2.319(1)	Ir–P(2)	2.315(1)
Ir–N	2.087(4)	Ir–C(19)	1.849(7)
P(1)–C(1)	1.835(6)	P(1)–C(7)	1.811(4)
P(1)–C(13)	1.829(4)	P(2)–C(20)	1.815(4)
P(2)–C(26)	1.822(5)	P(2)–C(32)	1.814(5)
F(1)–C(39)	1.332(6)	F(2)–C(39)	1.358(6)
F(3)–C(40)	1.329(7)	F(4)–C(40)	1.341(7)
N–C(38)	1.359(5)	N–C(41)	1.365(8)
C(38)–C(39)	1.537(8)	C(19)–O(19)	1.093(9)
C(38)–O(38)	1.197(6)	C(40)–C(41)	1.539(8)
C(39)–C(40)	1.510(8)	C(41)–O(41)	1.202(6)

Bond angles (°)

P(1)–Ir–P(2)	171.9	P(1)–Ir–N	90.3(1)
P(2)–Ir–N	93.2(1)	P(1)–Ir–C(19)	90.2(2)
P(2)–Ir–C(19)	86.7(2)	N–Ir–C(19)	177.0(2)
Ir–P(1)–C(1)	111.7(2)	Ir–P(1)–C(7)	115.0(1)
C(1)–P(1)–C(7)	105.5(2)	Ir–P(1)–C(13)	116.7(1)
C(1)–P(1)–C(13)	101.6(2)	C(7)–P(1)–C(13)	104.9(2)
Ir–P(2)–C(20)	118.0(2)	Ir–P(2)–C(26)	106.2(1)
C(20)–P(2)–C(26)	105.9(2)	Ir–P(2)–C(32)	117.2(2)
C(20)–P(2)–C(32)	100.8(2)	C(26)–P(2)–C(32)	107.9(2)
Ir–N–C(38)	124.0(3)	Ir–N–C(41)	123.8(3)
C(38)–N–C(41)	112.1(4)	P(1)–C(1)–C(2)	123.1(5)
P(1)–C(1)–C(6)	117.9(4)	P(1)–C(7)–C(8)	118.7(3)
P(1)–C(7)–C(12)	123.1(3)	P(1)–C(13)–C(14)	121.4(4)
P(1)–C(13)–C(18)	120.2(3)	P(2)–C(20)–C(25)	119.9(3)
P(2)–C(20)–C(21)	121.1(4)	P(2)–C(26)–C(31)	117.6(4)
P(2)–C(32)–C(33)	117.0(3)	P(2)–C(32)–C(37)	124.2(4)
Ir–C(19)–O(19)	178.6(7)	N–C(38)–C(39)	108.9(4)
N–C(38)–O(38)	128.0(5)	F(1)–C(39)–F(2)	107.0(4)
O(38)–C(38)–C(39)	123.0(4)	F(2)–C(39)–C(38)	108.5(5)
F(1)–C(39)–C(38)	112.7(5)	F(2)–C(39)–C(40)	110.3(5)
F(1)–C(39)–C(40)	113.0(5)	F(3)–C(40)–F(4)	107.8(5)
C(38)–C(39)–C(40)	105.3(4)	F(4)–C(40)–C(39)	112.6(4)
F(3)–C(40)–C(39)	111.2(5)	F(4)–C(40)–C(41)	110.7(5)
F(3)–C(40)–C(41)	111.8(4)	N–C(41)–C(40)	110.3(4)
C(39)–C(40)–C(41)	102.6(5)	C(40)–C(41)–O(41)	123.0(6)
N–C(41)–O(41)	126.7(5)		

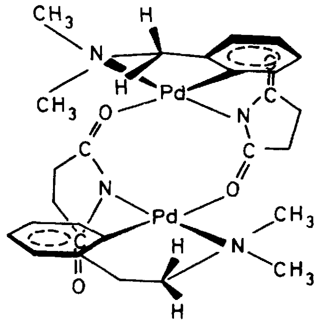


Figure 2. Proposed structure of $[\{Pd(o\text{-}C_6H_4CH_2NMe_2)(\mu\text{-}NCOC_2H_4CO)\}_2]$ (**7c**)

be expected to generate a U-shaped structure (Figure 2) in which the N-methyl groups and benzylic protons are inequivalent. In particular, one N-methyl group of each *ortho*-metallated ligand is directed inwards in this structure, and thus lies in the aromatic shielding zone of the other benzylic ligand. The outward-facing N-methyl group experiences no ring-current shielding, accounting then directly for the difference in chemical shift ($\delta\Delta = 0.92$ p.p.m.) between the two types of methyl group.

Table 4. Bond lengths and angles for $[\{Pd(o\text{-}C_6H_4CH{=}NPh)(\mu\text{-}NCOC_2H_4CO)\}_2]$ (**7a**), with estimated standard deviations in parentheses (* = symmetry-related atom)

Bond lengths (Å)

Pd(1)–O(1)	2.157(8)	C(1)–C(2)	1.393(18)
Pd(1)–N(1)	2.049(10)	C(2)–C(3)	1.361(19)
Pd(1)–N(2)*	2.032(10)	C(3)–C(4)	1.380(20)
Pd(1)–C(1)	1.972(12)	C(4)–C(5)	1.372(21)
O(1)–C(14)	1.234(15)	C(5)–C(6)	1.377(20)
O(2)–C(17)	1.209(16)	C(6)–C(1)	1.436(18)
N(2)–C(14)	1.361(16)	C(6)–C(7)	1.441(18)
N(2)–C(17)	1.401(16)	C(7)–N(1)	1.298(16)
C(14)–C(15)	1.520(19)	N(1)–C(8)	1.442(16)
C(15)–C(16)	1.526(20)	C(8)–C(9)	1.392(20)
C(16)–C(17)	1.552(20)	C(9)–C(10)	1.392(23)
		C(10)–C(11)	1.355(25)
Pd(1) ··· Pd(1)*	2.979 3(14)	C(11)–C(12)	1.372(26)
		C(12)–C(13)	1.401(23)
		C(13)–C(8)	1.398(20)

Bond angles (°)

O(1)–Pd(1)–N(1)	95.8(4)	Pd(1)–C(1)–C(2)	130.9(10)
O(1)–Pd(1)–N(2)*	89.3(4)	Pd(1)–C(1)–C(6)	113.2(9)
O(1)–Pd(1)–C(1)	176.3(4)	C(6)–C(1)–C(2)	116.0(11)
N(1)–Pd(1)–N(2)*	174.6(4)	C(1)–C(2)–C(3)	121.3(12)
N(1)–Pd(1)–C(1)	81.4(5)	C(2)–C(3)–C(4)	121.9(13)
C(1)–Pd(1)–N(2)*	93.6(5)	C(3)–C(4)–C(5)	119.3(14)
Pd(1)–O(1)–C(14)	126.9(8)	C(4)–C(5)–C(6)	119.8(13)
C(14)–N(2)–Pd(1)*	126.0(8)	C(5)–C(6)–C(1)	121.7(12)
C(17)–N(2)–Pd(1)*	123.3(8)	C(5)–C(6)–C(7)	124.9(12)
C(14)–N(2)–C(17)	110.7(10)	C(1)–C(6)–C(7)	113.1(11)
O(1)–C(14)–N(2)	125.6(11)	C(6)–C(7)–N(1)	118.1(12)
O(1)–C(14)–C(15)	123.3(11)	Pd(1)–N(1)–C(7)	113.2(8)
N(2)–C(14)–C(15)	111.2(11)	Pd(1)–N(1)–C(8)	127.1(8)
C(14)–C(15)–C(16)	105.1(11)	C(7)–N(1)–C(8)	119.5(11)
C(15)–C(16)–C(17)	102.9(11)	N(1)–C(8)–C(9)	122.0(12)
O(2)–C(17)–N(2)	124.7(12)	N(1)–C(8)–C(13)	117.4(12)
O(2)–C(17)–C(16)	125.4(12)	C(13)–C(8)–C(9)	120.5(13)
N(2)–C(17)–C(16)	109.9(11)	C(8)–C(9)–C(10)	118.8(14)
		C(9)–C(10)–C(11)	121.2(16)
		C(10)–C(11)–C(12)	120.5(17)
		C(11)–C(12)–C(13)	120.6(16)
		C(12)–C(13)–C(8)	118.5(14)

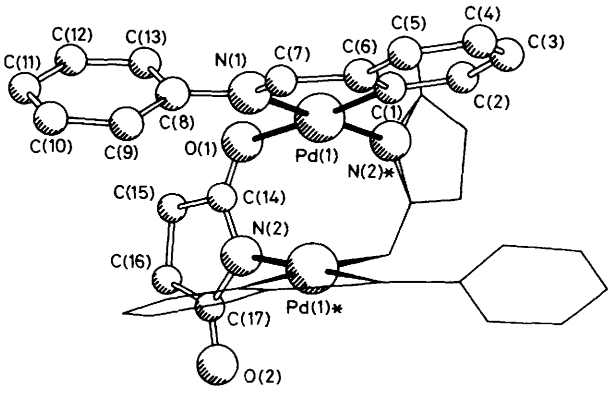


Figure 3. The structure of $[\{Pd(o\text{-}C_6H_4CH{=}NPh)(NCOC_2H_4CO)\}_2]$ (**7a**) (* = symmetry-related atom)

The structure of complex (**7a**) was determined crystallographically, and confirmed the proposed U-shaped conformation as shown in Figure 3. Selected bond lengths and angles are given in Table 4. The complex has crystallographically imposed C_2 symmetry, and the co-ordination planes of the two palladium

Table 5. Atomic co-ordinates (× 10^4) for $[\mathrm{Ir(CO)(\overline{NCOC_2F_4CO})(PPh_3)_2}]$ (**6c**), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ir	2 978(1)	745(1)	729(1)	C(19)	3 027(4)	1 036(4)	1 630(3)
P(1)	2 854(1)	2 651(1)	481(1)	O(19)	3 039(4)	1 205(4)	2 159(2)
P(2)	2 901(1)	−1 136(1)	985(1)	C(20)	3 825(3)	−1 729(4)	1 720(2)
F(1)	2 372(3)	−1 096(3)	−1 771(2)	C(21)	4 609(3)	−1 138(5)	2 045(3)
F(2)	2 019(2)	659(3)	−1 949(2)	C(22)	5 320(4)	−1 604(7)	2 569(3)
F(3)	4 028(2)	−625(3)	−1 234(2)	C(23)	5 264(4)	−2 660(7)	2 783(3)
F(4)	3 666(3)	1 069(4)	−1 603(2)	C(24)	4 509(5)	−3 292(5)	2 469(3)
N	2 995(2)	409(3)	−267(2)	C(25)	3 769(4)	−2 809(4)	1 932(3)
C(1)	2 052(3)	3 332(4)	803(2)	C(26)	1 903(3)	−1 290(4)	1 204(2)
C(2)	2 123(4)	4 434(5)	1 012(3)	C(27)	1 950(4)	−1 472(4)	1 883(3)
C(3)	1 487(4)	4 926(6)	1 214(4)	C(28)	1 193(4)	−1 410(5)	2 044(3)
C(4)	760(5)	4 323(6)	1 201(4)	C(29)	374(4)	−1 166(5)	1 528(3)
C(5)	676(4)	3 229(7)	1 005(4)	C(30)	303(4)	−997(5)	850(3)
C(6)	1 336(4)	2 715(5)	813(3)	C(31)	1 077(3)	−1 047(4)	685(3)
C(7)	3 892(3)	3 438(4)	863(2)	C(32)	2 819(3)	−2 139(4)	297(2)
C(8)	4 606(3)	2 956(4)	1 414(2)	C(33)	3 525(3)	−2 164(4)	57(2)
C(9)	5 365(3)	3 547(4)	1 748(3)	C(34)	3 515(4)	−2 890(4)	−471(3)
C(10)	5 464(3)	4 631(5)	1 538(3)	C(35)	2 809(4)	−3 576(5)	−770(3)
C(11)	4 791(4)	5 101(4)	990(3)	C(36)	2 097(4)	−3 586(5)	−544(3)
C(12)	4 003(4)	4 509(4)	648(3)	C(37)	2 090(3)	−2 868(4)	−8(3)
C(13)	2 404(3)	3 049(4)	−449(2)	C(38)	2 286(3)	−22(4)	−810(2)
C(14)	1 501(4)	3 219(4)	−806(3)	O(38)	1 570(2)	−312(4)	−809(2)
C(15)	1 159(4)	3 482(5)	−1 518(3)	C(39)	2 534(4)	−90(5)	−1 466(2)
C(16)	1 735(4)	3 567(5)	−1 876(3)	C(40)	3 514(4)	242(5)	−1 216(3)
C(17)	2 628(4)	3 391(4)	−1 535(3)	C(41)	3 709(4)	642(4)	−458(3)
C(18)	2 978(4)	3 138(4)	−823(2)	O(41)	4 399(3)	1 098(4)	−103(2)

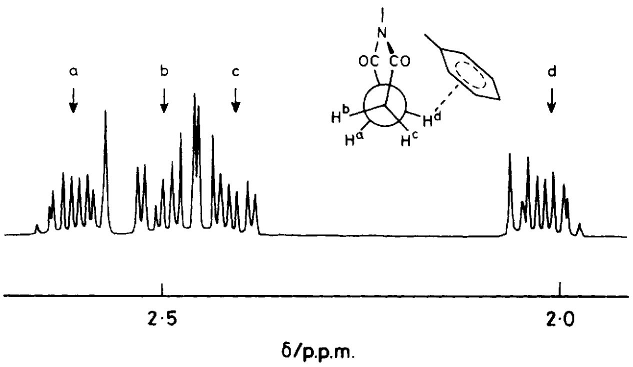


Figure 4. The 400-MHz ^{1}H n.m.r. spectrum (methylene region) of $[\{\mathrm{Pd}(o\text{-}\mathrm{C_6H_4CH{=}NPh})(\mu\text{-}\overline{\mathrm{NCOC_2H_4CO}})\}_2]$ (**7a**)

atoms form a dihedral angle of some 26°. The metal–metal distance of 2.98 Å is probably too great to allow significant Pd–Pd bonding, since well characterised Pd–Pd bonds[22] normally fall in the range 2.50—2.75 Å. The bridging succinimidato(1 −) ligands are essentially planar and are mutually inclined at an angle of 88.9°. The imino-N-phenyl ring lies adjacent to a succinimidato-methylene group, and, as a result, is twisted out of the co-ordination plane by some 48°. This proximity of phenyl and methylene groups in complex (**7a**) has a profound effect on the ^{1}H n.m.r. spectrum of the μ-succinimidato(1 −) ligand. In complex (**7c**), derived from benzyldimethylamine, the succinimidato-protons appear as a slightly broadened singlet at δ 2.68, whereas in the 400 MHz spectrum of (**7a**), these protons appear as a 32-line ABCX pattern (Figure 4), with one group of nine lines *ca.* 0.5 p.p.m. upfield from the rest, and assignable to the methylene proton immediately adjacent to the N-phenyl ring. Simulation of the spectrum using the program LAOCOON[23] suggested that the low-field nine-line multiplet is assignable to the proton geminal to the latter, the upper-field half of the central 14-line multiplet arises from the vicinal proton *cis* to the same reference proton, and the lower field part of the central multiplet is due to the corresponding *gauche* vicinal proton (Figure 4).

Experimental

Starting materials were prepared according to literature procedures. High resolution i.r. spectra were obtained using a Perkin-Elmer PE580 spectrometer, and other instrumentation and analytical techniques were as described in an earlier paper.[24]

Pentacarbonyl[*succinimidato*(1 −)]*manganese*(I), (**1**).—The thallium(I) salt of succinimide (0.60 g, 2.0 mmol) and bromo(pentacarbonyl)manganese (0.50 g, 1.8 mmol) were stirred in dry dichloromethane under N_2 for 16 h. The pale yellow precipitate was filtered off, and the complex isolated by evaporation of the solvent. Recrystallisation from dichloromethane–hexane yielded 0.25 g (47%) of moderately air-stable pale yellow crystals.

cis-[1,2-*Bis*(*diphenylphosphino*)*ethane*]*chloro*(*phenyl*)-*palladium*(II)-*Dichloromethane* (1/1).—The chelating diphosphine (3.0 mmol) and $[\mathrm{PdCl(Ph)(PPh_3)_2}]$ (2.7 mmol) were stirred in dry tetrahydrofuran under N_2 for 3 h. The precipitate was filtered off, dried, and recrystallised from dichloromethane–hexane to give 1.37 g (82%) of white crystals (Found: C, 56.6; H, 4.7; Cl, 15.1. Calc. for $\mathrm{C_{32}H_{29}ClPd{\cdot}CH_2Cl_2}$: C, 56.4; H, 4.5; Cl, 15.1%).

trans-*Phenyl*[*succinimidato*(1 −)]*bis*(*triphenylphosphine*)-*palladium*(II), (**2a**).—Succinimide (0.15 g, 1.5 mmol), triethylamine (4 cm^3), and *trans*-$[\mathrm{PdCl(Ph)(PPh_3)_2}]$ (1.0 g, 1.3 mmol) were stirred in dichloromethane (30 cm^3) for 2 h. The resulting solution was washed with water (2 × 50 cm^3) to remove $[\mathrm{NHEt_3}]\mathrm{Cl}$, dried over $\mathrm{MgSO_4}$, and evaporated to dryness. Recrystallisation from dichloromethane–hexane yielded 0.79 g (73%) of white crystals. Similarly were prepared (all in 70—90%

Table 6. Atomic co-ordinates (× 10^4) for the asymmetric unit of $[\{Pd(o\text{-}C_6H_4CH{=}NPh)(\overline{NCOC_2H_4CO})\}_2]\cdot CH_2Cl_2$ (**7a**), with estimated standard deviations in parentheses[a]

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pd(1)	1 202.1(8)	583.1(7)	2 420.1(5)	C(8)	2 233(10)	−455(10)	3 782(6)
O(1)	1 367(7)	1 599(6)	3 199(4)	C(9)	1 915(13)	−1 109(11)	4 190(8)
O(2)	−2 195(7)	1 888(6)	3 593(5)	C(10)	2 400(15)	−1 062(13)	4 883(7)
N(1)	1 818(7)	−489(8)	3 059(4)	C(11)	3 143(15)	−379(15)	5 163(7)
N(2)	−522(9)	1 556(7)	3 280(5)	C(12)	3 466(16)	267(12)	4 766(8)
C(1)	1 150(10)	−379(9)	1 742(6)	C(13)	3 013(13)	243(9)	4 065(7)
C(2)	928(11)	−325(8)	1 046(6)	C(14)	595(11)	1 863(8)	3 450(6)
C(3)	964(12)	−1 083(9)	668(7)	C(15)	786(12)	2 595(9)	3 992(7)
C(4)	1 174(12)	−1 945(10)	951(7)	C(16)	−410(12)	2 756(10)	4 103(7)
C(5)	1 374(13)	−2 041(9)	1 634(7)	C(17)	−1 180(12)	2 030(8)	3 639(6)
C(6)	1 385(11)	−1 279(9)	2 028(6)	C(18)*	5 160(60)	−069(17)	1 949(17)
C(7)	1 731(11)	−1 274(8)	2 753(7)	Cl(1)*	4 500(30)	873(11)	2 227(19)
				Cl(2)*	5 400(30)	−855(11)	2 617(19)

* Atoms C(18), Cl(1), and Cl(2) comprise the half-occupancy dichloromethane solvent molecule. The geometry of this solvent was constrained during refinement and the estimated standard deviations derive from those of the group parameters which were used to refine its position and orientation.

yield based on the corresponding chloro- or acetato-compounds) complexes (**2b**), (**2c**), (**3a**), (**3b**), (**4**), (**5a**), (**5b**), (**5c**), (**6a**), (**6b**), (**6c**), (**7a**), (**7b**), and (**7c**). Spectroscopic and analytical data are given in Tables 1 and 2 respectively.

Crystal Data for (**6c**).—$C_{41}H_{30}F_4IrNO_3P_2$, $M = 914.83$, monoclinic, $a = 15.995(1)$, $b = 11.915(2)$, $c = 20.453(3)$ Å, $\beta = 111.84(1)°$, $U = 3\,618(1)$ Å^3, space group $P2_1/n$, $Z = 4$, $D_c = 1.69$ g cm^{-3}. Yellow, air-stable prisms; crystal dimension, 0.25 mm ground sphere; $\mu(\text{Cu-}K_\alpha) = 84$ cm^{-1}, $\bar{\lambda} = 1.541\,78$ Å, $F(000) = 1\,800$.

Data Collection and Processing.—Nicolet R3m diffractometer (Imperial College), ω-scan method ($\theta \leqslant 50°$), graphite-monochromated Cu-K_α radiation; 3 572 independent observed reflections $[|F_o| > 3\sigma(|F_o|)]$, corrected for Lorentz and polarisation factors; empirical absorption based upon 314 azimuthal measurements.

Structure Analysis and Refinement.—The structure was solved by the heavy-atom method and the non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were idealised (C–H 0.96 Å), assigned isotropic thermal parameters $U(\text{H}) = 1.2\ U_{eq}$ (C) and allowed to ride on their parent carbons. Refinement was by block-cascade full-matrix least-squares to $R = 0.024$ $(R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|)$, $R' = 0.025$ $[w^{-1} = \sigma^2(F) + 0.000\,06\ F^2]$. The maximum residual electron density in the final ΔF map was 0.5 e Å^{-3} and the mean and maximum shifts/error in the final refinement cycle were 0.01 and 0.03 respectively. Computations were carried out on an Eclipse S140 computer using the SHELXTL program system.[25] Atomic co-ordinates are given in Table 5.

Crystal Data for (**7a**).—$C_{35}H_{30}Cl_2N_4O_4Pd_2$, $M = 854.35$, monoclinic, $a = 11.948(4)$, $b = 14.592(7)$, $c = 20.657(10)$ Å, $\beta = 105.79(3)°$, $U = 3\,464(3)$ Å^3, space group $C2/c$, $Z = 4$, $D_c = 1.64$ g cm^{-3}. Orange, air-stable needles; crystal dimensions 0.14 × 0.48 × 0.16 mm; $\mu(\text{Mo-}K_\alpha) = 12.22$ cm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, $F(000) = 1\,704$.

Data Collection and Processing.—Nicolet/Syntex R3 diffractometer (Sheffield), ω-scan method ($3.5 < 2\theta < 50°$), graphite-monochromated Mo-K_α radiation; 1 430 independent observed reflections $[I > 3\sigma(I)]$, corrected for Lorentz and polarisation effects.

Structure Analysis and Refinement.—Standard Patterson and Fourier methods followed by block-diagonal least-squares refinement. Hydrogen atoms were placed in calculated positions (C–H 0.98 Å) and included in structure factor calculations ($B = 7.0$ Å^2) but their positions were not refined. The disordered, half-occupancy molecule of dichloromethane was constrained (C–Cl 1.756 Å, Cl–C–Cl 104.3°) during the refinement, which converged to $R = 0.051$, with allowance for anisotropic thermal motion of non-hydrogen atoms, and for anomalous scattering of palladium and chlorine. Unit weights were used throughout. Scattering factors were taken from ref. 26, and computer programs formed part of the Sheffield *X*-ray system. Atomic co-ordinates are given in Table 6.

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