Reactions of Cyclobutenedione and Cyclopentenetrione with Zero-valent Nickel Triad Complexes of Isocyanide.[†] *X*-Ray Crystal Structures of (3—4-η-3,4-Diphenylcyclobut-3-ene-1,2-dione)- and (4—5-η-4,5-Diphenylcyclopent-4-ene-1,2,3-trione)-tris(t-butyl isocyanide)nickel[‡]

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$\mathrm{Hg[\{Pt_3(2,6\text{-}Me_2C_6H_3NC)_6\}_2]}$ reacts with 3,4-diphenylcyclobut-3-ene-1,2-dione, (**1**), to give the 4,5-diphenylplatinacyclopent-4-ene-2,3-dione complex, (**3a**). Reactions of (**1**) and 4,5-diphenylcyclopent-4-ene-1,2,3-trione, (**2**), with $\mathrm{[Pd_3(RNC)_6]}$ or $\mathrm{[Ni(RNC)_4]}$ give the olefinic complexes $\mathrm{[Pd(2,6\text{-}Me_2C_6H_3NC)_2\{Ph\overline{C{=}C(Ph)C(O)C}O\}]}$ (**4a**), $\mathrm{[Pd(RNC)_2\{Ph\overline{C{=}C(Ph)C(O)C(O)C}O\}]}$ [R = $\mathrm{2,6\text{-}Me_2C_6H_3}$ (**6a**) or $\mathrm{Bu^t}$ (**6c**)], $\mathrm{[Ni(RNC)_3\{Ph\overline{C{=}C(Ph)C(O)C}O\}]}$ [R = $\mathrm{2,6\text{-}Me_2C_6H_3}$ (**5a**) or $\mathrm{Bu^t}$ (**5c**)], and $\mathrm{[Ni(RNC)_3\{Ph\overline{C{=}C(Ph)C(O)C(O)C}O\}]}$ [R = $\mathrm{2,6\text{-}Me_2C_6H_3}$ (**7a**) or $\mathrm{Bu^t}$ (**7c**)]. The structures of (**5c**) and (**7c**) have been established by single-crystal *X*-ray analysis: both crystals are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions $a = 13.027(7)$, $b = 18.255(9)$, $c = 17.727(9)$ Å, and $\beta = 128.67(8)°$ for (**5c**) and $a = 19.679(13)$, $b = 16.499(11)$, $c = 11.694(8)$ Å, and $\beta = 106.14(7)°$ for (**7c**).

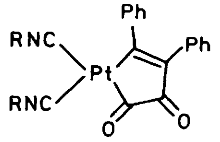
In spite of the ring tension characteristic of four-membered carbocyclic systems, cyclobutenedione and its derivatives exhibit high thermal stability. Cyclopentenetrione derivatives show unique chemical properties because of their arrangement of functional groups. These have extended the number of organic reactions of the cyclic diketones and triketones.[1,2] It is known that reactions of cyclobutenediones with low-valent transition metal phosphine complexes undergo carbon–carbon bond fission to give stable metallocyclic complexes or olefinic complexes, dependent on metals and reaction conditions.[3–6] The reaction of indan-1,2,3-trione with $\mathrm{[Pt(PPh_3)_4]}$ has been reported to give [2,2′-bis(indan-1,2,3-trionato)(2−)-$O^2O^{2'}$]-bis(triphenylphosphine)platinum.[7]

The reaction of diphenylcyclopropenone with a low-valent isocyanide complex is known,[8] but there is no report on the reaction of four- and five-membered polyketones with transition metal complexes of isocyanide. These polyketones have several possible sites for co-ordination: (i) the carbon–carbon double bond, (ii) one of the carbonyl groups, and (iii) a pair of vicinal carbonyl groups. Also, the possibility of an oxidative addition reaction cannot be excluded.

We report here the reactions of 3,4-diphenylcyclobut-3-ene-1,2-dione (**1**) and 4,5-diphenylcyclopent-4-ene-1,2,3-trione (**2**) with zero-valent metal (Ni, Pd, and Pt) complexes of isocyanide.

Results and Discussion

Reactions of (**1**).—Treatment of $\mathrm{Hg[\{Pt_3(2,6\text{-}Me_2C_6H_3NC)_6\}_2]}$ with (**1**) in benzene at 70 °C gives air-stable yellow crystals (**3a**) of formula $\mathrm{[Pt(2,6\text{-}Me_2C_6H_3NC)_2(Ph_2C_4O_2)]}$. The i.r. spectrum shows two peaks each for terminal isocyanides and carbonyls [2 172, 2 149 (N≡C), 1 658, 1 655 cm^{-1} (C=O)]. The ^{1}H n.m.r. spectrum in $\mathrm{CDCl_3}$ shows two resonances at δ 2.58 and 2.08 assignable to the 2,6-Me$_2$ groups. These spectroscopic data suggest a 4,5-diphenylplatinacyclopent-4-ene-2,3-dione structure.



(**3**)

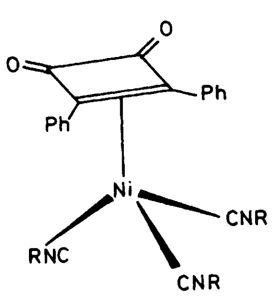
The similar complex $\mathrm{[Pt(2,4,6\text{-}Bu^t_3C_6H_2NC)_2(Ph_2C_4O_2)]}$ (**3b**) is obtained from the reaction with $\mathrm{[Pt_3(2,4,6\text{-}Bu^t_3C_6H_2NC)_6]}$. Closely similar compounds have been reported by Kemmitt and co-workers:[3a] the reaction of $\mathrm{[Pt(PPh_3)_4]}$ with 3,4-disubstituted cyclobut-3-ene-1,2-dione derivatives underwent cleavage of a C–C bond to give the platinacyclopentenedione derivatives.

The reaction of (**1**) with $\mathrm{[Pd_3(2,6\text{-}Me_2C_6H_3NC)_6]}$ at room temperature gives yellow crystals of $\mathrm{[Pd(2,6\text{-}Me_2C_6H_3NC)_2(Ph_2C_4O_2)]}$ (**4a**). Complex (**4a**) reacts with iodine to give $\mathrm{[Pd(2,6\text{-}Me_2C_6H_3NC)_2I_2]}$ and (**1**) in quantitative yields, indicating that a cyclobutenedione group remains unchanged in the molecule. The i.r. spectrum for (**4b**) shows four peaks at 2 174, 2 151 (N≡C), 1 735, 1 687, and 1 663 cm^{-1} (C=O) for terminal isocyanide and carbonyl groups. The carbonyl stretching frequencies are higher in energy by 10—80 cm^{-1} from those of the platinum complexes. It is known that the olefinic complexes of platinum exhibit carbonyl stretching frequencies in the range 1 730—1 690 cm^{-1} and platinacyclic complexes, values in the range 1 680—1 650 cm^{-1}.[3a] From these results, we suggest the olefinic structure for (**4a**).

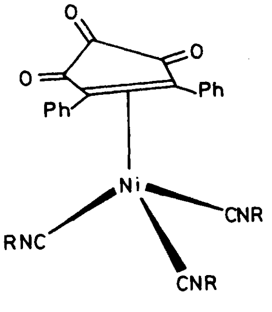
The reaction of (**1**) with tetrakis(isocyanide)nickel complexes gives orange-yellow or reddish orange crystals of (**5**), formulated as $\mathrm{[Ni(RNC)_3(Ph_2C_4O_2)]}$ [R = $\mathrm{2,6\text{-}Me_2C_6H_3}$ (**5a**) or $\mathrm{Bu^t}$ (**5c**)]. However, the reaction with $\mathrm{[Ni(2,4,6\text{-}Bu^t_3C_6H_2NC)_4]}$, having bulky trisubstituted phenyl groups, results in recovery of the starting compounds, indicating the low reactivity of this complex. The reaction of (**5a**) with iodine gives $\mathrm{[Ni(2,6\text{-}Me_2C_6H_3NC)_2I_2]}$ and (**1**) in quantitative yields, suggesting the presence of the cyclobutenedione group.

[†] Taken as 'Studies on Interactions of Isocyanides with Transition Metal Complexes. Part 32.' For Part 31, see preceding paper.

[‡] *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.



(5c)



(7c)

The structure of (5) was determined by an *X*-ray analysis of (5c), which was found to have a tetrahedral geometry around the nickel atom (see below). The spectroscopic results are in good agreement with the structure. The i.r. spectra of (5) show two peaks near 2 150 cm^{-1} and one peak near 1 685 cm^{-1}, assignable to terminal isocyanides and carbonyls respectively. The carbonyl band is lower in energy by *ca.* 80—100 cm^{-1} than that of the unco-ordinated diketone, suggesting the presence of back-bonding from the nickel atom to the olefin. The ^{1}H n.m.r. spectra show the presence of only one kind of isocyanide group. This type of complex has been prepared by the reaction of five-co-ordinated (2,2′-bipyridine)dicarbonyl(η-phenylacetylene)-nickel with t-butyl isocyanide.[5]

The carbonyl bands of the nickel complexes are lower in energy than those of palladium analogues. This is not only responsible for difference of geometry but also for the number of electron-donating isocyanide ligands in the molecule.

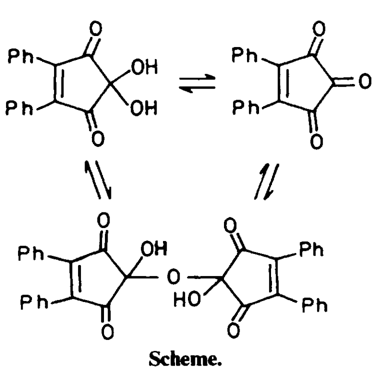
Reactions of (2).—When [$Pd_3(RNC)_6$] is treated with (2) at room temperature, orange or orange-brown crystals of [$Pd(RNC)_2(Ph_2C_5O_3)$] [R = 2,6-$Me_2C_6H_3$ (**6a**) or Bu^t (**6c**)] are obtained in fairly good yield. The i.r. spectrum shows two ν(N≡C) bands at 2 280—2 160 cm^{-1} and three carbonyl bands at 1 740—1 650 cm^{-1}. The carbonyl band pattern is similar to that of the unco-ordinated triketone, although the bands are slightly lower in energy than in the latter. The ^{1}H n.m.r. spectrum shows the presence of only one kind of isocyanide ligand. These results suggest an olefin structure similar to those of cyclobutenedione complexes of palladium. The reaction with [$Ni(RNC)_4$] gives red or dark red crystals of [$Ni(RNC)_3$-($Ph_2C_5O_3$)] [R = 2,6-$Me_2C_6H_3$ (**7a**) or Bu^t (**7c**)]. The structure was determined to involve a tetrahedral geometry around the Ni atom by an *X*-ray analysis of (**7c**) (see below). In the i.r. spectra, the carbonyl band pattern is similar to that of the unco-ordinated triketone, but the stretching frequencies appear to lower frequency by 40—100 cm^{-1}. This trend is closely similar to that for the cyclobutenedione complexes of nickel.

It has been noted from the i.r. spectra of various 1,2-disubstituted cyclopentenetriones that the electron deficiency of the five-membered ring caused by the electron-withdrawing effect of the carbonyl groups is compensated by the electron donation from the substituents attached to the olefinic double bond.[2] The appearance of carbonyl bands at lower frequencies than for unco-ordinated triketone shows high back-bonding from nickel to the five-membered ring. The effect influences the reactivity of the co-ordinated triketone. The unco-ordinated triketone (**2**) readily reacts with H_2O to give a hydrate, with which the compound is considered to be in equilibrium (Scheme).[2a] However, the olefinic complexes are insensitive to water.

Table 1. Bond distances (Å) and bond angles (°) for (**5c**) and (**7c**)*

(5c)		(7c)	
(*a*) Distances			
Ni–C(17)	1.880(17)	Ni–C(18)	1.926(15)
Ni–C(23)	1.961(12)	Ni–C(24)	1.953(13)
Ni–C(29)	1.922(10)	Ni–C(30)	1.915(16)
Ni–m	1.907	Ni–m	1.930
Ni–C(3)	2.038(15)	Ni–C(3)	2.076(12)
Ni–C(4)	2.043(9)	Ni–C(4)	2.046(13)
C(17)–N(18)	1.153(22)	C(18)–N(19)	1.118(19)
C(23)–N(24)	1.139(16)	C(24)–N(25)	1.140(17)
C(29)–N(30)	1.139(13)	C(30)–N(31)	1.127(21)
C(1)–C(2)	1.542(19)	C(1)–C(2)	1.504(21)
C(1)–C(4)	1.516(18)	C(1)–C(5)	1.493(21)
C(2)–C(3)	1.514(18)	C(2)–C(3)	1.501(19)
C(3)–C(4)	1.452(18)	C(3)–C(4)	1.449(21)
C(1)–O(1)	1.210(18)	C(4)–C(5)	1.484(19)
C(2)–O(2)	1.201(13)	C(1)–O(1)	1.234(16)
		C(2)–O(2)	1.223(19)
		C(5)–O(5)	1.238(20)
(*b*) Bond angles			
C(17)–Ni–C(23)	105.4(6)	C(18)–Ni–C(24)	103.5(6)
C(17)–Ni–C(29)	107.0(6)	C(18)–Ni–C(30)	106.9(6)
C(23)–Ni–C(29)	107.8(6)	C(24)–Ni–C(30)	101.0(6)
C(17)–Ni–m	120.2	C(18)–Ni–m	121.5
C(23)–Ni–m	100.4	C(24)–Ni–m	101.0
C(29)–Ni–m	114.8	C(30)–Ni–m	119.2
Ni–C(17)–N(18)	177.1(12)	Ni–C(18)–N(19)	171.6(13)
Ni–C(23)–N(24)	176.5(13)	Ni–C(24)–N(25)	179.6(12)
Ni–C(30)–N(31)	172.5(13)	Ni–C(30)–N(31)	174.8(13)
C(17)–N(18)–C(19)	177.9(13)	C(18)–N(19)–C(20)	169.2(16)
C(23)–N(24)–C(25)	176.5(13)	C(24)–N(25)–C(26)	173.6(13)
C(29)–N(39)–C(31)	172.5(13)	C(30)–N(31)–C(32)	175.5(14)
C(2)–C(1)–C(4)	88.2(10)	C(2)–C(1)–C(5)	107.2(11)
C(1)–C(2)–C(3)	88.4(10)	C(3)–C(2)–C(1)	106.5(11)
C(2)–C(3)–C(4)	91.7(10)	C(4)–C(3)–C(2)	109.1(11)
C(1)–C(4)–C(3)	91.7(10)	C(1)–C(5)–C(4)	107.9(12)
C(4)–C(1)–O(1)	135.6(12)	C(2)–C(1)–O(1)	125.4(12)
C(2)–C(1)–O(1)	135.5(12)	C(5)–C(1)–O(1)	127.2(13)
C(3)–C(2)–O(2)	135.9(13)	C(1)–C(2)–O(2)	125.9(13)
C(1)–C(2)–O(2)	135.5(13)	C(3)–C(2)–O(2)	127.4(13)
		C(1)–C(5)–O(5)	125.5(13)
		C(4)–C(5)–O(5)	126.5(13)

* m = Mid-point of the C(3)–C(4) (olefinic) bond.



Scheme.

Structures of (*3,4-Diphenylcyclobut-3-ene-1,2-dione*)*tris*(*t-butyl isocyanide*)*nickel*, (**5c**), *and* (*4,5-Diphenylcyclopent-4-ene-1,2,3-trione*)*tris*(*t-butyl isocyanide*)*nickel*, (**7c**).—The molecular geometries of (**5c**) and (**7c**) are shown in Figures 1 and 2. Bond distances and angles are given in Table 1. The co-ordination geometries about the Ni atom in (**5c**) and (**7c**) are approximately tetrahedral, having mean values of 107 and 112° for the C–Ni–C and C–Ni–m (mid-point of the olefinic bond) angles in (**5c**) and 104 and 114° for those in (**7c**). The Ni–C–N

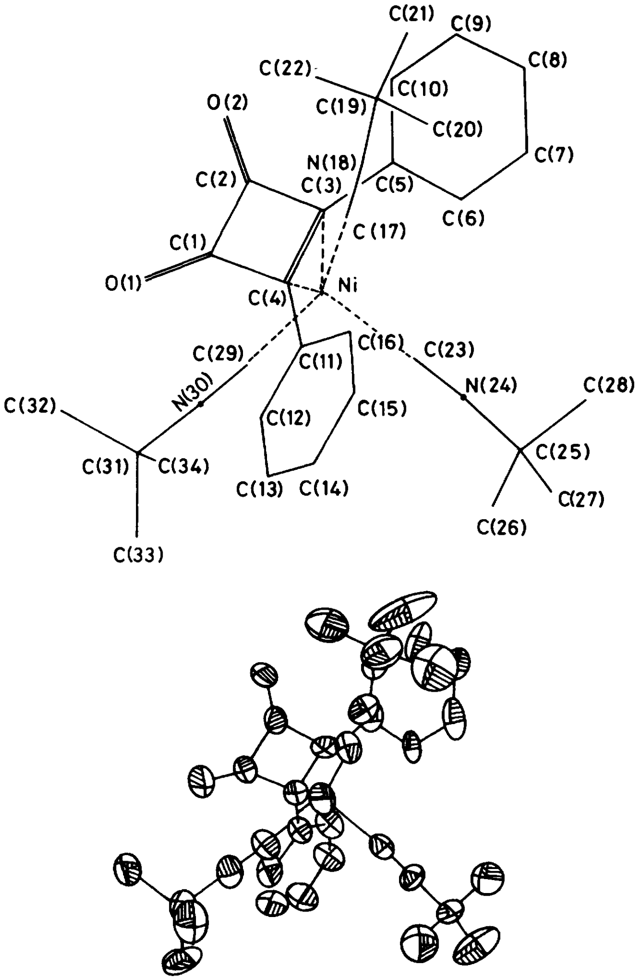


Figure 1. Molecular structure of (**5c**)

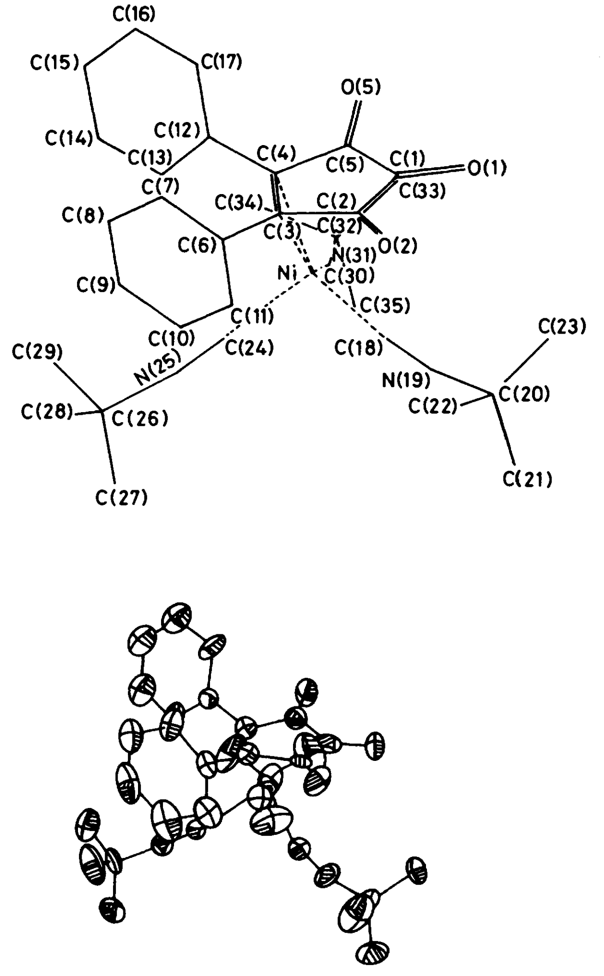


Figure 2. Molecular structure of (**7c**)

and C–N–C bond angles are nearly linear. The arrangement of the three Bu^{t}NC groups around the Ni atom in both complexes is such that one of them rests between the two phenyl groups. The Ni–C (terminal) bond lengths in (**5c**) and (**7c**) range from 1.88 to 1.96 Å, longer than the corresponding bond lengths in the nickel isocyanide complexes [Ni(Bu^{t}NC)$_2$(tcne)] (tcne = tetracyanoethylene),[9] having an approximately trigonal geometry which is responsible for crowding around the Ni atom. The Ni–C (olefinic) distances are 2.04 and 2.04 Å in (**5c**) and 2.05 and 2.08 Å in (**7c**), showing that these carbons are nearly equidistant from the Ni atom and are symmetrically linked to it. These distances are not significantly different from the Ni–C distances of 1.93 and 2.01 Å in [Ni(Bu^{t}NC)$_2$(tcne)] and [Ni(PPh$_3$)$_2$(CH$_2$CH$_2$)][9,10] and those (2.12 and 2.00 Å) in 3-methyl-4-phenylcyclobut-3-ene-1,2-dionebis(triphenylphosphine)platinum.[7] The olefinic C–C distances are 1.45 Å for both (**5c**) and (**7c**); compound (**1**) has an olefinic bond length of 1.358 Å.[11] On co-ordination there is significant lengthening of the olefinic bond due to back-donation from metal into olefinic antibonding orbitals.

Table 2. Crystal data for (**5c**) and (**7c**)

	(**5c**)·0.5C$_6$H$_6$	(**7c**)·C$_6$H$_6$
Formula	C$_{31}$H$_{37}$N$_3$NiO$_2$·0.5C$_6$H$_6$	C$_{32}$H$_{37}$N$_3$NiO$_3$·C$_6$H$_6$
M	580.7	647.7
System	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	13.027(7)	19.679(13)
b/Å	18.255(9)	16.499(11)
c/Å	17.727(9)	11.694(8)
β/°	128.67(8)	106.14(7)
U/Å^3	3 291	3 629
D_c/g cm^{-3}	1.17	1.19
D_m/g cm^{-3}	1.17	
Z	4	4
μ(Cu-K_α)/cm^{-1}	11.9	11.7
Crystal size (mm)	0.2 × 0.3 × 0.8	0.2 × 0.3 × 0.5
Total no. of reflections	4 119	4 794
No. of observed reflections	2 678	2 000
2θ$_{max.}$	110	110
F(000)	1 236	1 376

A comparison of the structure of the cyclobutenedione group in (**5c**) with those found in 3-phenylcyclobut-3-ene-1,2-dione, (**8**),[12] and in 3-cyclohexenylcyclobut-3-ene-1,2-dione, (**9**),[13] shows, in addition to the significant elongation of the C(3)–C(4) olefinic bond, a slight elongation of the C(1)–C(4) and C(2)–C(3) lengths of up to 0.05 Å in (**5c**). However, it is not certain whether the difference is caused by the co-ordination to the metal atom or by the attachment of the additional phenyl group to the double bond. The molecules (**8**) and (**9**) are roughly planar, whereas in (**5c**) and (**7c**), the phenyl groups are twisted around the bonds connecting the phenyl rings to the cyclobutene or cyclopentene ring, in which the dihedral angles

Table 3. Atomic co-ordinates for complex (5c)

Atom	x	y	z	Atom	x	y	z
Ni	0.021 1(2)	0.215 2(1)	0.406 0(1)	N(18)	0.175 9(9)	0.765 5(5)	0.066 8(7)
O(1)	0.029 6(8)	0.548 6(4)	0.201 8(6)	C(19)	0.290 3(12)	0.785 1(8)	0.073 4(9)
O(2)	0.286 9(7)	0.641 5(4)	0.265 9(6)	C(20)	0.240 5(17)	0.840 2(9)	−0.010 4(13)
C(1)	0.058 8(11)	0.612 3(6)	0.212 7(8)	C(21)	0.391 2(17)	0.817 1(14)	0.174 9(14)
C(2)	0.179 4(11)	0.656 4(6)	0.241 1(8)	C(22)	0.343 8(15)	0.714 5(9)	0.061 6(13)
C(3)	0.113 1(10)	0.724 9(6)	0.240 8(7)	C(23)	0.145 2(10)	0.295 6(6)	0.443 0(8)
C(4)	−0.001 0(11)	0.683 4(6)	0.212 8(8)	N(24)	0.221 7(8)	0.338 6(5)	0.463 4(7)
C(5)	0.177 7(11)	0.794 8(6)	0.288 9(8)	C(25)	0.314 2(12)	0.393 1(7)	0.483 1(10)
C(6)	0.105 5(13)	0.855 8(6)	0.281 1(8)	C(26)	0.406 5(16)	0.357 0(10)	0.466 4(15)
C(7)	0.174 5(15)	0.921 3(7)	0.329 2(10)	C(27)	0.390 0(18)	0.416 5(12)	0.590 3(12)
C(8)	0.311 3(14)	0.924 3(7)	0.381 1(9)	C(28)	0.237 6(16)	0.455 9(8)	0.411 1(14)
C(9)	0.380 1(14)	0.865 1(7)	0.388 4(10)	C(29)	0.125 8(11)	0.362 5(6)	−0.003 3(8)
C(10)	0.314 6(11)	0.800 2(7)	0.342 0(8)	N(30)	0.184 5(9)	0.410 4(5)	0.047 0(7)
C(11)	−0.104 0(11)	0.690 6(6)	0.222 2(8)	C(31)	0.255 8(12)	0.471 1(6)	0.111 9(9)
C(12)	−0.213 1(13)	0.645 2(7)	0.167 3(10)	C(32)	0.171 8(14)	0.541 1(7)	0.059 6(10)
C(13)	−0.310 6(14)	0.646 7(9)	0.178 9(11)	C(33)	0.388 1(13)	0.477 5(9)	0.131 6(12)
C(14)	−0.298 0(14)	0.693 5(9)	0.246 7(10)	C(34)	0.272 5(15)	0.456 5(8)	0.203 2(10)
C(15)	−0.189 8(14)	0.739 0(9)	0.302 6(10)	C(B1)	0.045 5(15)	−0.055 8(8)	0.067 4(11)
C(16)	−0.088 8(13)	0.738 3(7)	0.291 0(9)	C(B2)	0.081 7(15)	0.016 2(8)	0.098 9(11)
C(17)	0.095 8(11)	0.746 7(6)	0.071 6(8)	C(B3)	0.037 1(15)	0.071 5(7)	0.031 7(11)

Table 4. Atomic co-ordinates for complex (7c)

Atom	x	y	z	Atom	x	y	z
Ni	0.184 6(1)	0.127 0(1)	0.112 4(2)	C(20)	0.072 2(8)	−0.079 6(8)	0.226 8(13)
C(1)	0.284 6(7)	0.031 3(8)	0.244 5(12)	C(21)	0.000 9(8)	−0.107 6(10)	0.143 6(15)
C(2)	0.246 7(7)	0.077 4(8)	0.319 6(12)	C(22)	0.061 2(10)	−0.048 4(11)	0.346 1(16)
C(3)	0.244 0(7)	0.164 2(8)	0.280 2(11)	C(23)	0.130 3(8)	−0.145 3(9)	0.244 0(16)
C(4)	0.283 5(7)	0.172 6(7)	0.192 9(11)	C(24)	0.122 0(7)	0.221 4(8)	0.080 6(12)
C(5)	0.312 9(7)	0.092 2(8)	0.174 9(13)	N(25)	0.085 6(6)	0.276 7(6)	0.062 6(10)
O(1)	0.294 1(5)	−0.042 7(5)	0.247 3(9)	C(26)	0.045 9(8)	0.353 3(8)	0.040 8(13)
O(2)	0.226 4(5)	0.049 5(6)	0.401 3(8)	C(27)	−0.027 2(8)	0.336 9(10)	−0.042 5(16)
O(5)	0.356 7(5)	0.078 3(6)	0.118 8(10)	C(28)	0.041 2(11)	0.383 8(11)	0.162 8(16)
C(6)	0.217 7(7)	0.229 2(8)	0.345 1(11)	C(29)	0.089 7(10)	0.411 0(10)	−0.013 2(16)
C(7)	0.258 0(8)	0.298 5(8)	0.380 0(12)	C(30)	0.196 6(8)	0.107 3(8)	−0.042 3(13)
C(8)	0.232 6(9)	0.356 6(9)	0.450 1(13)	N(31)	0.205 4(6)	0.101 4(7)	−0.113 1(10)
C(9)	0.169 5(9)	0.342 8(9)	0.480 7(13)	C(32)	0.221 9(9)	0.098 4(9)	−0.250 3(13)
C(10)	0.130 1(9)	0.273 5(10)	0.443 8(14)	C(33)	0.279 6(11)	0.032 3(12)	−0.238 7(18)
C(11)	0.153 4(8)	0.214 2(9)	0.374 8(12)	C(34)	0.250 0(13)	0.183 4(12)	−0.269 1(18)
C(12)	0.315 4(7)	0.248 7(7)	0.159 5(12)	C(35)	0.152 9(11)	0.076 4(14)	−0.343 0(16)
C(13)	0.278 0(9)	0.299 7(9)	0.072 1(14)	C(B1)	0.512 7(13)	0.060 2(11)	0.650 7(16)
C(14)	0.311 8(9)	0.369 7(10)	0.046 6(14)	C(B2)	0.440 8(14)	0.045 4(15)	0.592 9(19)
C(15)	0.382 4(9)	0.387 0(10)	0.108 9(15)	C(B3)	0.400 1(9)	0.117 3(19)	0.553 9(17)
C(16)	0.421 2(10)	0.332 0(11)	0.193 0(16)	C(B4)	0.434 7(13)	0.187 4(14)	0.564 3(18)
C(17)	0.387 1(8)	0.260 4(10)	0.219 0(15)	C(B5)	0.500 0(14)	0.196 3(15)	0.163 0(20)
C(18)	0.124 6(7)	0.042 0(8)	0.142 7(12)	C(B6)	0.540 1(10)	0.135 6(15)	0.658 7(16)
N(19)	0.096 2(6)	−0.009 2(7)	0.172 5(10)				

between the phenyl rings and cyclobutene or cyclopentene ring are 19.4 and 4.05° for (**5c**) and 42.4 and 77.4° for (**7c**). Both substitutuent carbons attached to C=C [C(5) and C(11) in (**5c**) and C(6) and C(12) in (**7c**)], and the carbonyl oxygen atoms on the immediate neighbours [O(1) and O(2) in (**5c**) and O(2) and O(5) in (**7c**)] significantly deviate from the mean plane, away from the Ni atom. It is seen that the twist of the phenyl groups occurs to avoid very short contacts between them and the bending of the bonds around the olefinic bond occurs to release the repulsions against the Ni atom. Non-bonded interatomic short contacts within each complex and between the complex molecules are few.

Experimental

General Procedures and Physical Measurements.—The reactions were carried out under an atmosphere of nitrogen. Melting points were taken on a Laboratory Devices Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded on a Shimazu IR-27G instrument and n.m.r. spectra were obtained on JEOL C-60HL and Varian HA-100B spectrometers. Molecular weights were measured by a vapour-pressure osmometer.

Materials.—The isocyanides,[14] and compounds (**1**)[15] and (**2**)[2a] were prepared by procedures described in the literature. Platinum, palladium, and nickel isocyanide complexes were prepared according to published methods.[16–18]

Reactions of $Hg[\{Pt_3(2,6\text{-}Me_2C_6H_3NC)_6\}_2]$ *with* (**1**).—To a solution of $Hg[\{Pt_3(2,6\text{-}Me_2C_6H_3NC)_6\}_2]$ (0.05 g, 0.017 mmol) in benzene (10 cm^3) was added (**1**) (0.035 g, 0.15 mmol) at room temperature. After stirring for 1 h, the mixture was treated with charcoal. Removal of the solvent and crystallization from benzene–hexane gave orange-yellow crystals of (**3a**) (0.062 g, 88.0%), m.p. 212—213 °C (decomp.) (Found: C, 59.2; H, 4.10; N, 4.05. Calc. for $C_{34}H_{28}N_2O_2Pt$: C, 59.05; H, 4.00; N, 4.05%). N.m.r. ($CDCl_3$): δ 2.08 (s, Me), 2.58 (s, Me), −7.0 (aromatic protons).

Reaction of $[Pt_3(2,4,6\text{-}Bu^t{}_3C_6H_2NC)_6]$ *with* (**1**).—A mixture of $[Pt_3(2,4,6\text{-}Bu^t{}_3C_6H_2NC)_6]$ (0.07 g, 0.032 mmol) and (**1**) (0.052 g, 0.22 mmol) was refluxed in benzene for 2 h. The mixture was chromatographed on alumina containing 10% H_2O. Elution with CH_2Cl_2 gave a yellow-orange solution. Crystallization from benzene–hexane yielded yellow orange crystals of (**3b**) (0.074 g, 79.4%), m.p. 207—209 °C (decomp.) (Found: C, 66.90; H, 7.15; N, 2.80. Calc. for $C_{54}H_{68}N_2O_2Pt$: C, 66.7; H, 7.05; N, 2.90%). I.r. (Nujol): 2 174, 2 151 (N≡C), 1 735, 1 687, 1 663 cm^{-1} (C=O). N.m.r. ($CDCl_3$): δ 1.24 (s, 4-Bu^t), 1.29 (s, 4-Bu^t), 1.30 (s, 2,6-Bu^t), 1.49 (s, 2,6-$Bu^t{}_2$), 7.02 (aromatic protons), 7.21 (s, 3,5-H), 7.31 (s, 3,5-H).

Nickel complexes were prepared by similar procedures to those described for the preparation of the platinum complex. $[Ni(2,6\text{-}Me_2C_6H_3NC)_3\{PhC{=}C(Ph)C(O)CO\}]$ (**5a**), reddish orange-yellow, yield 75%, m.p. 133—134 °C (decomp.) [Found: C, 75.65; H, 5.30; N, 6.20%; *M* (C_6H_6), 678. Calc. for $C_{43}H_{37}N_3NiO_2$: C, 75.25; H, 5.45; N, 6.10%; *M*, 687]. I.r. (KBr): 2 150, 2 112 (N≡C), 1 688 cm^{-1} (C=O). N.m.r. ($CDCl_3$): δ 2.27 (s br, 2,6-Me_2), *ca.* 7.4 (aromatic protons). $[Ni(Bu^tNC)_3\{PhC{=}C(Ph)C(O)CO\}]$ (**5c**), orange-yellow, yield 83%, m.p. 105—111 °C (decomp.) (Found: C, 68.65; H, 6.80; N, 7.80. Calc. for $C_{31}H_{37}N_3NiO_2$: C, 68.65; H, 6.90; N, 7.70%). I.r. (KBr): 2 187, 2 166 (N≡C), 1 688 cm^{-1} (C=O). N.m.r. ($CDCl_3$): δ 1.42 (s br, Bu^t), *ca.* 7.7 (aromatic protons).

Reaction of $[Pd_3(2,6\text{-}Me_2C_6H_3NC)_6]$ *with* (**2**).—A mixture of $[Pd_3(2,6\text{-}Me_2C_6H_3NC)_6]$ (0.04 g, 0.036 mmol) and (**2**) (0.034 g, 0.13 mmol) was stirred in benzene at room temperature. After 1 h, the mixture was filtered and hexane was added to the filtrate to give orange-brown crystals of (**6a**) (0.015 g, 23%), m.p. 149—151 °C (decomp.) (Found: C, 66.35; H, 4.65; N, 4.10. Calc. for $C_{35}H_{28}N_2O_3Pd$: C, 66.60; H, 4.45; N, 4.10%). I.r. (KBr): 2 278, 2 288 (N≡C), 1 733, 1 690, 1 655 cm^{-1} (C=O). N.m.r. ($CDCl_3$): δ 2.29 (s, 2,6-Me_2), *ca.* 7.3 (aromatic protons). $[Pd(Bu^tNC)_2\{PhC{=}C(Ph)C(O)C(O)CO\}]$ (**6c**), orange, yield 91%, m.p. 147—150 °C (decomp.) [Found: C, 60.75; H, 5.20; N, 5.20; *M* (C_6H_6), 531. Calc. for $C_{27}H_{28}N_2O_3Pd$: C, 60.60; H, 5.30; N, 5.25%; *M*, 535] I.r. (KBr): 2 180, 2 167 (N≡C), 1 733, 1 681, 1 651 cm^{-1} (C=O). Electronic spectrum (CH_2Cl_2): $\lambda_{max.}$ 257 (ε 17 100), 338 (sh, 9 130) $dm^3\ mol^{-1}\ cm^{-1}$). N.m.r. ($CDCl_3$): δ 1.34 (s, Bu^t), *ca.* 7.4 (aromatic protons).

Nickel complexes were prepared by similar procedures to those described for the palladium complexes. $[Ni(2,6\text{-}Me_2C_6H_3NC)_3\{PhC(Ph)C(O)C(O)CO\}]$ (**7a**), orange, yield 84%, m.p. 149—152 °C (decomp.) [Found: C, 74.15; H, 5.25; N, 5.65%; *M* (C_6H_6) 727. Calc. for $C_{44}H_{37}N_3NiO_3$: C, 73.95; H, 5.20; N, 5.90%; *M*, 714]. I.r. (KBr): 2 161, 2 139 (N≡C), 1 677, 1 661, 1 628 cm^{-1} (C=O). N.m.r. ($CDCl_3$): δ 2.30 (s, 2,6-Me_2), *ca.* 7.4 (aromatic protons). Electronic spectrum (CH_2Cl_2): $\lambda_{max.}$ 402 (ε 5 600), 307 (23 800), 281 nm (23 900 $dm^3\ mol^{-1}\ cm^{-1}$). $[Ni(Bu^tNC)_3\{PhC{=}C(Ph)C(O)C(O)CO\}]\cdot 0.5CH_2Cl_2$ (**7c**)·$0.5CH_2Cl_2$, orange, yield 87%, m.p. 125—130 °C (decomp.) [Found: C, 64.0; H, 6.30; N, 7.05%; *M* (C_6H_6), 625. Calc. for $C_{32.5}H_{38}ClN_3NiO_3$: C, 63.7; H, 6.25; N, 6.85%; *M*, 578]. I.r. (Nujol): 2 190, 2 170 (N≡C), 1 665, 1 621 cm^{-1} (C=O). N.m.r. ($CDCl_3$): δ 1.38 (s, Bu^t), 5.28 (s, CH_2), *ca.* 7.3 (aromatic protons).

Reaction of (**4a**) *with Iodine.*—To a solution of (**4a**) (0.05 g, 0.083 mmol) in benzene (15 ml) was added iodine (0.03 g, 0.12 mmol) at room temperature. After 1 h, the solvent was removed and hexane was added to give orange crystals of $[Pd(2,6\text{-}Me_2C_6H_3NC)_2I_2]$ (0.049 mg, 95%). Further crystallization of the mother-liquor gave 18 mg (93%) of (**1**). A similar reaction between (**5c**) and iodine gave $[Ni(Bu^tNC)_2I_2]$ and (**1**) in 95% and 94% yields, respectively.

X-*Ray Crystallographic Studies.*—Crystals of (**5c**) and (**7c**) for *X*-ray analysis were obtained by recrystallization from benzene. Crystal data are given in Table 2. The lattice constants and intensity data were measured with a Rigaku four-circle *X*-ray diffractometer using nickel-filtered Cu-K_α radiation (λ = 1.5418 Å). The integrated intensities were measured by the θ—2ω scan method. The reflections having net intensities $I > 2\sigma(I)$ were taken as observed and were corrected for Lorentz polarization factors. No absorption correction was applied.

The structures were solved by the heavy-atom method and refined by block-diagonal least-squares methods using the program HBLS.[19] All atoms were refined isotropically. The final *R* values were 0.090 (2 678 reflections) for (**5c**) and 0.085 (2 000 reflections) for (**7c**). No hydrogen atom contributions were taken into account, unit weights were assigned for these in both cases. Atomic scattering factors for Ni, C, N, and H were taken from ref. 20. The final atomic co-ordinates are given in Tables 3 and 4.

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