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Organomercury(II) and diorganothallium(III) derivatives of 4-acylpyrazol-5-ones

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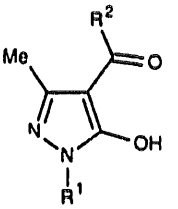
Abstract

The synthesis and characterization of four organomercury derivatives of 1-phenyl-3-methyl-4-acyl-5-pyrazolones (L), RHgL (R = Me, Ph; acyl = acetyl, benzoyl), are described. The report includes the crystal structure of one compound, PhHg[1-Ph-3-Me-4-PhCO-5-C_2N_2CO], which represents the first crystallographically authenticated mercury β-diketonate bonded to the metal through oxygen, and also the first structural report on an organomercury β-diketonate. For comparison, the two diphenylthallium derivatives of the same two pyrazolone ligands have also been prepared.

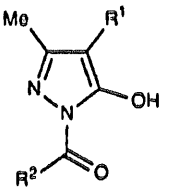
Keywords: Mercury; Thallium; β-Diketone; Acylpyrazol-5-ones; X-ray diffraction

1. Introduction

While the coordination chemistry of 4-acyl-5-pyrazolones (**I**) is well developed with respect to inorganic receptors [1–3], organometallic derivatives of this class of ligand are still rather limited. Early work on complexes containing rhodium and iridium olefin moieties [4] have subsequently been expanded to include di-organotin compounds [5–8]. We have recently contributed to this field by structurally characterizing the first triorganotin 5-pyrazolone, as well as reporting organotin complexes of the isomeric 1-acyl-5-pyrazolone ligand (**II**) [9]. We now report the successful synthesis of organomercury derivatives of **I**, along with two organothallium analogues for comparison.



I



II

Mercury, as a soft metal [10], has a low affinity for oxygen, and crystal structure determinations of mercury β-diketonates such as bis(dipivaloylmethyl)mercury(II) [$^tBuC(O)CHC(O)^tBu]_2Hg$ [11,12], (dipivaloylmethyl)-mercuric acetate [$^tBuC(O)CHC(O)^tBu$]HgOAc [13] and

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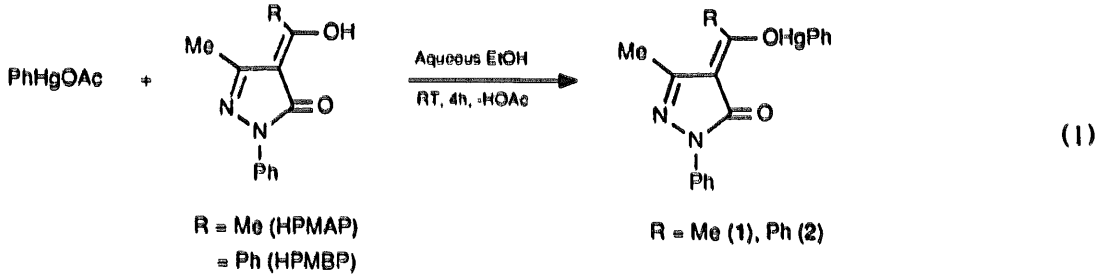
3,3-bis(chloromercuric)-2,4-pentanedione $(MeCO)_2C(HgCl)_2$ [14] have shown that in the solid state mercury is bonded to carbon. Secondary Hg · · · O interactions are always observed in these mercuric β-diketonates, though in the case of [^{t}BuC(O)CHC(O)^{t}Bu]HgOAc [13] it is the oxygen atoms of the acetate groups that are responsible and not those of the dipivaloylmethyl group.

Methylmercury complexes of β-diketonates such as $(MeCO)_2CH_2$, $(CF_3CO)_2CH_2$ and $(CF_3CO)CH_2(COCH_3)$, synthesized either from reacting Me_2Hg and the diketone at refluxing temperature or from the diketone and $MeHgN(SiMe_3)_2$ at −80 °C, have been inferred to incorporate both Hg–C and Hg–O bonded species [15]. Spectroscopic data also suggest similar mixed coordination modes for products of the reactions between phenylmercuric halides and $(PhCO)_2CH_2$ [16]. Mercury's antipathy for coordinated oxygen is highlighted by the structures containing analogous monothio β-diketone and β-ketoiminato ligands, where coordination is primarily *S,S-* and *C,N-* in nature, respectively [17,18]. Surprisingly, no crystal structures of any organomercury β-diketonates have been published so far, nor have any of the crystallographically authenticated mercury β-diketonates to date been found to contain the *O,O*-chelating mode of bonding so common for this ligand group. This report establishes precedent in both of these areas. In contrast, organothallium β-diketone complexes are well established; for example, $Me_2Tl(acac)$ has the normally *O,O*-chelated ligand, though weak intermolecular Tl · · · O interactions expand the coordination number about thallium to six [19]. Thus, for comparison, we have also synthesised the first organothallium derivatives of 4-acylpyrazolones, whose properties are reported herein.

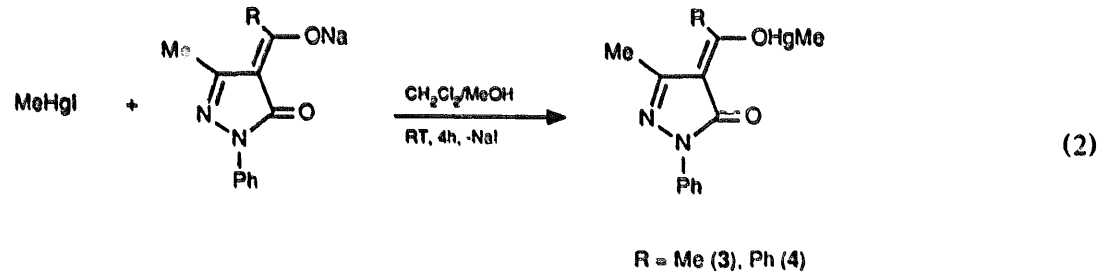
2. Results and discussion

2.1. Synthesis and spectroscopy

A comprehensive survey of the synthetic routes which have been employed for the isolation of mercuric β-diketonate compounds has been published in a recent review [20]. In the present study, phenylmercury(II) pyrazol-5-onates (**1**, **2**) were made by treating phenylmercury acetate in aqueous ethanol with equimolar quantities of the appropriate pyrazol-5-one (Eq. (1)). The analogous methylmercury(II) derivatives (**3**, **4**) were made by stirring equimolar quantities of methylmercuric iodide and the sodium pyrazol-5-onate in dichloromethane–methanol (3:1) (Eq. (2)). Yields of the phenylmercury derivatives (ca. 90%) were higher than those of the methylmercury analogues (ca. 40%).



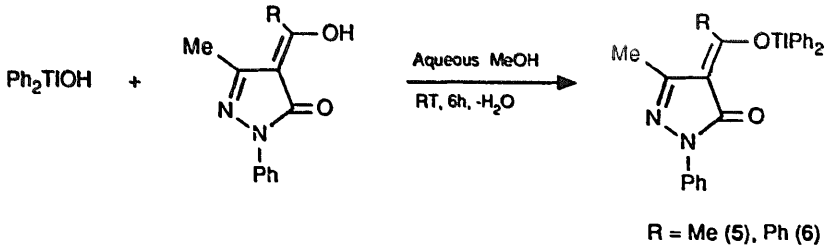
(1)



(2)

The new compounds are brown (**1**, **2**) or yellow (**3**, **4**) high melting solids, soluble in various organic solvents (e.g. toluene, chloroform, methanol and ether). They are stable in air, but for long storage should be kept in a vacuum desiccator or under nitrogen.

The analogous diphenylthallium species **5** and **6** have also been prepared, from Ph_2TlOH and the protonated ligands HPMAP and HPMBP (Eq. (3)):



R = Me (5), Ph (6) (3)

Important IR bands for the compounds **1–6** have been assigned by comparison with spectra of the free ligands and with data reported in earlier literature for pyrazol-5-onate complexes [3,6,7]. In the spectra of the six compounds the ν(O–H) band of the ligands disappears, indicating deprotonation. The shift of the ν(C=O) absorption band from 1630–1675 cm^{-1} in the free ligands to 1579–1626 cm^{-1} in the complexes, and the absence of the broad absorption band due to ν(OH · · · O), suggest that both the carbonyl groups are involved in bonding to the two metals through the oxygen atoms. The absence of ν(–NH–) signal between 3080–3600 cm^{-1} in the IR spectra of the complexes rules out the possibilities of any amino–diketo tautomeric form coordinating through one or two carbonyl groups or forming a coordinate link to mercury through the nitrogen atom of a secondary amino group.

By analogy with the assignments for other methylmercury compounds, $\delta(CH_3)$ and ν(Hg–C) in the complexes have been assigned to bands in the regions 1170–1190 cm^{-1} and 520–550 cm^{-1} respectively.

The ^1H and ^{13}C NMR spectra of compounds **1–6** incorporate the same features as those of their respective ligands, except for the disappearance of the broad O–H band of the enol forms of the ligand between 10.2–10.7 ppm in the ^1H NMR spectrum. This suggests that the organometallic unit is coordinated to the oxygen atom of the deprotonated enol form of the ligand. The sharp singlets at ca. $\delta = 0.75$ ppm in the spectra of methylmercury(II) derivatives are flanked by ^{199}Hg satellites arising from $^2J(^{199}Hg–H)$ coupling of 169.2 (**3**) and 179.5 Hz (**4**). These are larger than for the *C*-bonded β-diketonate complex MeHg(acac) (135 Hz), though with the much more electronegative β-diketo-

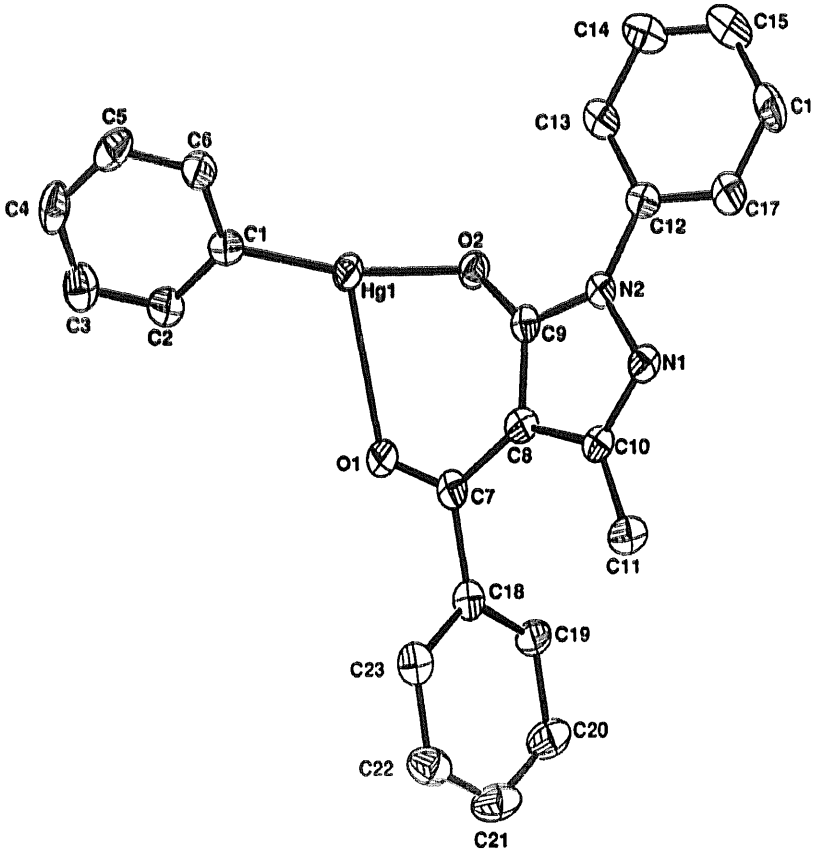


Fig. 1. The asymmetric unit of **2** showing the atomic labelling scheme used in the text and tables. Ellipsoids illustrated are at the 30% probability level.

Table 1
Selected geometric data (Å, deg) for 2

Bond lengths			
O(1)-Hg(1)	2.585(9)	O(2)-Hg(1)	2.087(7)
C(1)-Hg(1)	2.040(11)	N(2)-N(1)	1.394(9)
C(10)-N(1)	1.312(11)	C(9)-N(2)	1.363(10)
C(12)-N(2)	1.419(11)	C(7)-O(1)	1.237(10)
C(9)-O(2)	1.289(10)	C(8)-C(7)	1.449(12)
C(18)-C(7)	1.511(14)	C(9)-C(8)	1.420(13)
C(10)-C(8)	1.440(12)	C(11)-C(10)	1.489(13)
Bond angles			
O(2)-Hg(1)-O(1)	78.3(3)	C(1)-Hg(1)-O(1)	112.1(4)
C(1)-Hg(1)-O(2)	168.6(3)	C(10)-N(1)-N(2)	106.9(7)
C(9)-N(2)-N(1)	111.2(7)	C(12)-N(2)-N(1)	118.6(7)
C(12)-N(2)-C(9)	129.9(8)	C(7)-O(1)-Hg(1)	121.7(7)
C(9)-O(2)-Hg(1)	119.4(6)	C(2)-C(1)-Hg(1)	120.4(8)
C(6)-C(1)-Hg(1)	121.9(8)	C(8)-C(7)-O(1)	122.2(9)
C(18)-C(7)-O(1)	119.8(8)	C(18)-C(7)-C(8)	118.0(8)
C(9)-C(8)-C(7)	124.6(9)	C(10)-C(8)-C(7)	130.5(8)
C(10)-C(8)-C(9)	104.9(8)	O(2)-C(9)-N(2)	123.4(8)
C(8)-C(9)-N(2)	106.3(8)	C(8)-C(9)-O(2)	130.3(7)
C(8)-C(10)-N(1)	110.7(9)	C(11)-C(10)-N(1)	119.0(8)
C(11)-C(10)-C(8)	130.2(8)		

nate hfac the coupling increases dramatically (248 Hz), an observation which has been associated with a change to Hg–O bonding [15].

The positions of the ^{13}C resonances of the *N*-phenyl carbon atoms appear to be unaffected by complexation, although those of the coordinating carbonyl groups are deshielded in the complexes. This is consistent with the binding of the organomercury group to the enol oxygen of the pyrazol-5-onates.

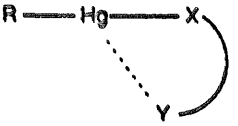
The coupling constants $^{1}J(^{13}C-^{199}Hg)$ and $^{2}J(^{1}H-^{199}Hg)$ have been used by others to quantify, in a relative sense, the stability constant β of methylmercury(II) compounds [21–23]. Although these coupling constants can be potentially unreliable measures of β when ligands of different donor group are compared [23], structurally similar ligands possessing the same donor group are reflected by a linear decrease in J as log β increases. That is, a strongly bound ligand trans to the R group in HgRL compounds weakens the Hg–C bond, decreasing its s character and hence ^{n}J. On these grounds, the values of $^{1}J(^{13}C-^{199}Hg)$ (**3**: 1102; **4**: 1123 Hz) and $^{2}J(^{1}H-^{199}Hg)$ discussed earlier suggest the following stability sequence for the methylmercury(II) derivatives: HgMePMAP > HgMePMBP.

The position of $\delta(^{199}Hg)$ for the phenylmercury derivatives **1** and **2** (−1157.5, −1026.2 ppm) are further upfield than those for the methylmercury analogues **3** and **4** (−828.4, −755.6 ppm) respectively, consistent with the recent observations for $RHg(S_2PEt_2)$ ($\delta(^{199}Hg)$, R = Me: −591.7; R = Ph: −898.4 ppm) [24]. Moreover, the ^{199}Hg NMR resonances for **1**–**4** are significantly shifted from those of these Hg–S bonded compounds, suggesting coordination to an element of significantly different electronegativity, i.e. oxygen not carbon.

2.2. *Crystal Structure of (1-phenyl-3-methyl-4-benzoylpyrazol-5-onato)phenylmercury(II) (2)*

Fig. 1 shows the asymmetric unit of **2** and the numbering scheme used in the text. Selected distances and angles are given in Table 1. The crystal structure involves discrete molecules with no Hg · · · Hg or other intermolecular interactions (Hg(1)–Hg(1'): 4.429 Å). The mercury atom is coordinated to the C(1) atom of the phenyl group (Hg(1)–C(1): 2.040(11) Å) and to the O(2) atom of the 4-benzoylpyrazol-5-onate (Hg(1)–O(2): 2.087(7) Å). The C(1)–Hg–O(2) moiety is nonlinear (168.6(3)°), arising from additional coordination

Table 2
Comparative geometric data (Å, deg) for **2** and related mercury compounds



Compound	Hg–C	Hg–X	Hg–Y	C–Hg–X
2 [a]	2.040	2.087 [b]	2.585 [c]	168.6
$(HgCl)_2(acac)$ [d]	2.11, 2.14 [e]	2.30 [f]	2.82, 3.01, 3.02 [c]	172, 174
$Hg(DPM)_2$ [g]	2.13 [e]	2.18 [e,h]	2.70 [c]	170
Hg(DPM)OAc [i]	2.11 [e]	2.10 [h,j]	2.74, 2.82, 2.82 [c]	175
$Hg(trop)_2$ [k]	2.30 [h,l]	2.50 [c,l]		
$Hg(SPDM)_2$ [m,n]		2.351, 2.337 [o]	2.654, 2.708 [c]	178.4 [p]
$[(Hg(HNDPM)]_1]^{1+}$ [q,r]	2.096, 2.106, 2.109 [e]	2.087, 2.090, 2.073 [s]	2.519, 2.532, 2.549 [c]	175.1, 175.5, 171.8

[a] This work. [b] X = O. [c] Y = O. [d] Ref. [14]. [e] β-Diketone carbon. [f] X = Cl. [g] Ref. [25]. [h] X = C. [i] Ref. [26]. [j] Acetate oxygen. [k] Ref. [27]. [l] Mean values. [m] SPDM = monthio-dipivalolylmethane. [n] Ref. [18]. [o] X = S. [p] < S–Hg–S. [q] HNDPM = 4-imino-dipivalolylmethane. [r] Ref. [18]. [s] X = N.

of the metal to O(1) (Hg(1)–O(1): 2.585(9) Å). Although the deviation from 180° is relatively modest in itself, it is slightly larger than normally observed and indicates that the Hg–O(1) bond is relatively strong. For example, in $[\{^tBuC(NH)CHC(O)^tBuHg\}_3]^{3+}$ although each mercury is weakly three-coordinate through apparently short, chelating C=O · · · Hg interactions (2.519–2.532 Å) the C–Hg–N units are relatively unperturbed (171.8–175.1°) [18]. Similarly, one mercury centre in $(HgCl)_2C(CO.Me)_2$ is also three-coordinate from an intermolecular Hg · · · O bond (2.82 Å) that has little impact on the C–Hg–Cl angle (172°) [14]. A comparison of Hg–O bond lengths in related compounds is shown in Table 2. Weak secondary Hg–O distances have been reported to be between 2.700–2.956 Å, whereas an average distance of 2.669 Å was quoted for typical Hg–O coordinate bonds in a recently determined *O,S*-crown ether complex [28]. Hence, the Hg(1)–O(1) distance of 2.585 Å observed in **2** is short; indeed, it is one of the shortest such bonds reported to date, and by inference relatively strong. The asymmetry in the Hg–O bonds is reflected in the C–O bonds of the ligand (C(7)–O(1): 1.237(10); C(9)–O(2): 1.289(10) Å), with the short Hg–O bond being associated with the longer C–O bond and vice versa, as expected.

The approximately 'T-shaped' geometry of ligands about the mercury results from distortion of the nominally linear C–Hg–O unit by additional β-diketone chelation. **2** is the first example of an *O,O*-chelating β-diketonate mercury complex, and presumably arises from the blocking of the preferred carbon site (C(8)) by its incorporation into a heterocyclic ring. Interestingly, steric hindrance alone of the latter carbon is insufficient to prevent bonding at this site [17]. The closest structural analogue of **2** is mercury(II) bis-(tropolonate), in which each ligand chelates the mercury in an *O,O*-manner (Hg–O: 2.30, 2.50 Å), though one of the two tropolone groups also acts in an additional bridging manner, thus raising the coordination number at the metal to six [27]. In **2**, the six-membered HgO_2C_3 ring adopts a half-chair conformation (Fig. 2) with a fold angle of 31.6°, while the pyrazole ring to which it is fused is planar (maximum displacements from least squares plane: C(9) −0.013, N(2) 0.011 Å).

3. Experimental

Methylmercury(II) iodide, phenylmercury(II) acetate and 1-phenyl-3-methylpyrazol-5-one were of commercial origin. 1-Phenyl-3-methyl-4-acetylpyrazol-5-one (HPMAP) and 1-phenyl-3-methyl-4-benzoyl pyrazol-5-one (HPMBP) were prepared by the methods of Jensen [1] and Okafor [29] and converted to their sodium salts according to a literature procedure [30]. Ph_2TlOH was prepared from Ph_2TlCl [31] by the method reported by Garcia Tasende et al. [32].

Spectra were recorded on the following instruments: Jeol GX270 (^1H, ^{13}C NMR), GX400 (^{199}Hg NMR), Perkin Elmer 599B (IR). NMR spectra were recorded in $CDCl_3$ unless indicated otherwise.

3.1. Synthesis of (1-phenyl-3-methyl-4-acetylpyrazol-5-onato)phenylmercury(II) PhHg(PMAP) (1)

A suspension of phenylmercuric acetate (0.68 g, 0.2 mmol) in ethanol (30 ml) was added to a stoichiometric quantity of HPMAP (0.44 g, 0.2 mmol) dissolved in ethanol (20 ml). The mixture was stirred for 4 h at room temperature and the solvent removed under vacuum to give brown solid, which was recrystallized from toluene (0.81 g, 86%), m.p. 194 °C. Found (Calc. for $C_{18}H_{16}HgN_2O_2$): C, 42.8 (42.5); H, 3.3 (3.3); N, 5.5 (5.6)%. IR (Nujol mull; cm^{-1}): 1579s ν(C=O), 538w ν(Ph–Hg). ^1H NMR: 1.75 (s, 3H, 3-methyl), 1.58 (s, 3H, 4-acetyl Me), 6.40–7.32 (m, 10H, C_6H_5). ^{13}C NMR: 14.9 (3-methyl), 27.2 (4-acetyl Me), 102.5 (C-4), 146.4 (C-3), 161.7 (4-acetyl CO), 191.1 (C-5) 136.4, 126.6, 135.2, 127.3 ($C_{i,o,m,p}H_5Hg$), 135.3, 121.1, 127.5, 124.4 ($C_{i,o,m,p}H_5(N\text{-}1)$). ^{199}Hg NMR (0.5 M EtOH): −1157.5 ppm.

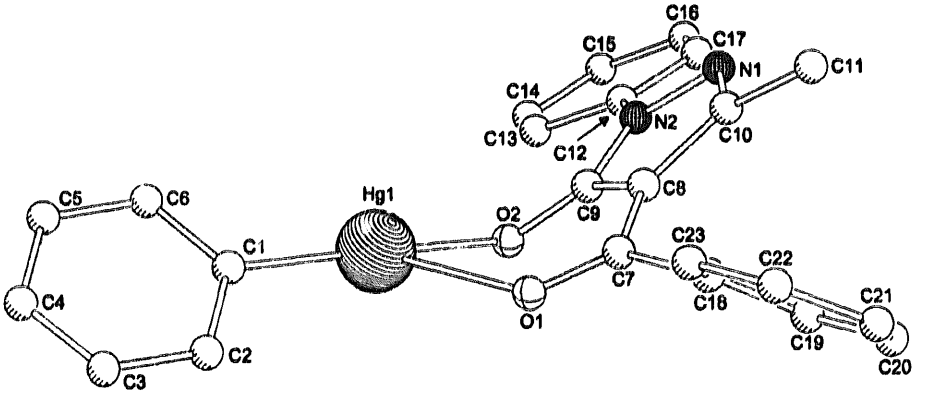


Fig. 2. A view of **2** showing the half-chair conformation of the HgO_2C_3 chelate ring and the planarity of the fused pyrazole unit.

3.2. Synthesis of (1-phenyl-3-methyl-4-benzoylpyrazol-5-onato)phenylmercury(II) PhHg(PMBP) (2)

This compound was prepared in a manner analogous to that described for (1), by stirring ethanol solutions of equimolar quantities of phenylmercuric acetate (0.64 g, 0.2 mmol) and HPMBP (0.56 g, 0.2 mmol) for 4 h at room temperature. The product was recrystallised from toluene, yielding yellow crystals suitable for X-ray diffraction measurements (1.11 g, 92%), m.p. 160 °C. Found (Calc. for $C_{23}H_{18}HgN_2O_2$): C, 49.5 (49.8); H, 3.3 (3.3); N, 5.0 (5.1)%. IR (Nujol mull; cm^{-1}): 1595s ν(C=O), 546w ν(Ph–Hg). ^1H NMR: 1.78 (s, 3H, 3-methyl), 7.20–7.87 (m, 15H, C_6H_5). ^{13}C NMR: 16.3 (3-methyl), 138.2, 128.9, 128.8, 136.8 (4-benzoyl, $C_{i,o,m,p}H_5$), 104.8 (C-4), 149.0 (C-3), 163.1 (4-benzoyl CO), 193.7 (C-5), 140.7, 126.0, 140.2, 129.0 ($C_{i,o,m,p}H_5Hg$), 138.2, 121.9, 130.8, 127.8 ($C_{i,o,m,p}H_5$(N-1)). ^{199}Hg NMR (0.5 M EtOH): −1026.2 ppm.

3.3. Synthesis of (1-phenyl-3-methyl-4-acetylprazol-5-onato)methylmercury(II), MeHg(PMAP) (3)

A suspension of methylmercuric iodide (0.90 g, 0.3 mmol) in dichloromethane (40 ml) was added to a stoichiometric quantity of NaPMAP (0.72 g, 0.3 mmol) dissolved in ethanol (25 ml). The mixture was stirred for 4 h at room temperature and the resulting suspension was filtered to give a yellow-brown filtrate. The solution was then evaporated to dryness on a rotary evaporator, to give a brown solid product. Recrystallization was effected from toluene–dichloromethane (1:3) mixture. The brown solid formed was filtered off under suction and vacuum dried (0.52 g, 40%), m.p. 172 °C (dec.). Found (Calc. for $C_{13}H_{24}HgN_2O_2$): C, 36.2 (36.3); H, 3.5 (3.3); N, 6.3 (6.5)%. IR (Nujol mull; cm^{-1}): 1626s ν(C=O), 538w ν(Me–Hg). ^1H NMR: 1.71 (s, 3H, 3-methyl), 1.52 (s, 3H, 4-acetyl Me), 0.85 (s, 3H, MeHg), 7.22–7.75 (m, 5H, C_6H_5); $^2J(^1H–Hg)$ = 169.2 Hz. ^{13}C NMR: 17.7 (3-methyl), 7.8 (MeHg), 28.4 (4-acetyl Me), 166.4 (4-acetyl CO), 103.5 (C-4), 149.1 (C-3), 189.7 (C-5), 117.7, 118.1, 128.5, 121.9 ($C_{i,o,m,p}H_5$(N-1)); $^1J(^{13}C–Hg)$ = 1102 Hz. ^{199}Hg NMR (0.5 M EtOH): −828.4 ppm.

3.4. Synthesis of (1-phenyl-3-methyl-4-benzoylpyrazol-5-onato)methylmercury(II), MeHg(PMBP) (4)

This compound was prepared in a manner analogous to that described for (3), by stirring ethanol–dichloromethane solutions of equimolar quantities of methylmercuric iodide (0.90 g, 0.3 mmol) and NaPMBP (0.90 g, 0.3 mmol) at room temperature. The bright yellow filtrate obtained on filtering the mixture at the end of 4 h reaction time was evaporated to dryness under vacuum to yield a yellow product which was recrystallized from acetonitrile and dried under vacuum (0.56 g, 38%), m.p. 156 °C. Found (Calc. for $C_{18}H_{16}HgN_2O_2$): C, 43.8 (43.6); H, 3.7 (3.8); N, 5.7 (5.7)%. IR (Nujol mull; cm^{-1}): 1618s ν(C=O), 524w ν(Me–Hg). ^1H NMR: 1.82 (s, 3H, 3-methyl), 0.72 (s, 3H; MeHg), 7.18–7.68 (m, 15H, C_6H_5); $^2J(^1H–Hg)$ = 179.5 Hz. ^{13}C NMR: 17.0 (3-methyl), 5.6 (MeHg), 137.6, 128.4, 128.8, 137.4 (4-benzoyl, $C_{i,o,m,p}H_5$), 162.7 (4-benzoyl CO), 103.3 (C-4), 147.5 (C-3), 190.7 (C-5), 120.2, 127.4, 132.5, 137.7 ($C_{i,o,m,p}H_5$(N-1)); $^1J(^{13}C–Hg)$ = 1123 Hz. ^{199}Hg NMR (0.5 M EtOH): −755.6 ppm.

3.5. Synthesis of (1-phenyl-3-methyl-4-acetylpyrazol-5-onato)diphenylthallium(III), Ph_2Tl(PMAP) (5)

An aqueous solution of diphenylthallium hydroxide (1.89 g, 5 mmol), obtained by treating diphenylthallium chloride with an aqueous suspension of freshly prepared Ag_2O, was added to an equimolar methanolic solution of HPMAP. The mixture was stirred at room temperature for 6 h, the solvents removed in vacuo, and the residue recrystallized from chloroform to yield 5 as a brown solid (1.15 g, 40%) m.p. 51 °C. Found (Calc. for $C_{24}H_{21}N_2O_2Tl$): C, 50.8 (50.3); H, 3.8 (3.7); N, 5.3 (4.9)%. IR (Nujol mull; cm^{-1}): 1590s ν(C=O). ^1H NMR: 1.42 (s, 3H, 3-methyl), 1.41 (s, 3H, 4-acetyl Me), 7.24–7.74 (m, 15H, C_6H_5). ^{13}C NMR: 14.9 (3-methyl), 27.9 (4-acetyl Me), 104.6 (C-4), 136.9 (C-3), 161.6 (4-acetyl CO), 192.4 (C-5) 120.9, 124.6, 128.7, 134.6 ($C_{i,o,m,p}H_5$(N-1)), 125.0, 125.4, 126.8, 127.2, 136.7, 136.9, 138.3, 138.6 ($C_{i,o,m,p}H_5Tl$).

3.6. Synthesis of (1-phenyl-3-methyl-4-benzoylpyrazol-5-onato)diphenylthallium(III), Ph_2Tl(PMBP) (6)

This compound was prepared in the same manner as 5, from 5 mmol quantities of Ph_2TlOH and HPMBP. The crude product was recrystallized from 1:1 hexane–chloroform to yield 6 as a greenish-yellow material (1.44 g, 45%) m.p. 58 °C. Found (Calc. for $C_{29}H_{23}N_2O_2Tl$): C, 54.7 (54.8); H, 3.9 (3.6); N, 4.6 (4.4)%. IR (Nujol mull; cm^{-1}): 1598s ν(C=O). ^1H NMR: 1.78 (s, 3H, 3-methyl), 6.80–7.64 (m, 20H, C_6H_5). ^{13}C NMR: 15.2 (3-methyl), 137.9, 128.9, 128.8, 136.6 (4-benzoyl, $C_{i,o,m,p}H_5$), 104.2 (C-4), 133.0 (C-3), 160.4 (4-benzoyl CO), 192.8 (C-5), 121.3, 122.7, 126.9, 133.8 ($C_{i,o,m,p}H_5$(N-1)), 123.2, 124.9, 126.4, 126.5, 137.2, 137.3, 138.2, 138.9 ($C_{i,o,m,p}H_5Tl$).

3.7. X-ray data collection and structure determination of (1-phenyl-3-methyl-4-benzoylpyrazol-5-onato)phenylmercury(II), [HgPh(PMBP)] (2)

A crystal of approximate dimensions 0.2 × 0.2 × 0.2 mm was used for data collection.

Table 3
Fractional atomic coordinates ($\times 10^4$) for **2**

	x	y	z
Hg(1)	1812.9(3)	950.7(3)	559.1(2)
N(1)	5170(7)	−1019(7)	−1005(4)
N(2)	4450(6)	74(6)	−963(4)
O(1)	1464(7)	−1370(6)	303(4)
O(2)	2484(6)	773(5)	−492(3)
C(1)	1091(9)	1479(8)	1526(5)
C(2)	−103(8)	972(8)	1734(5)
C(3)	−636(10)	1369(10)	2364(6)
C(4)	−35(11)	2301(10)	2785(5)
C(5)	1162(11)	2790(9)	2602(5)
C(6)	1728(9)	2364(8)	1981(5)
C(7)	2211(9)	−1955(8)	−76(4)
C(8)	3272(8)	−1369(8)	−441(5)
C(9)	3318(8)	−97(8)	−609(4)
C(10)	4469(8)	−1878(8)	−710(4)
C(11)	5020(9)	−3152(8)	−657(5)
C(12)	4875(8)	1120(8)	−1345(4)
C(13)	4376(9)	2281(9)	−1225(5)
C(14)	4781(11)	3276(10)	−1628(6)
C(15)	5731(10)	3134(11)	−2117(6)
C(16)	6252(10)	1976(10)	−2218(5)
C(17)	5826(9)	980(9)	−1845(5)
C(18)	2001(8)	−3320(8)	−186(5)
C(19)	1825(9)	−3805(8)	−891(5)
C(20)	1618(10)	−5042(10)	−997(7)
C(21)	1550(10)	−5784(9)	−388(8)
C(22)	1680(10)	−5302(10)	321(7)
C(23)	1895(8)	−4058(9)	422(5)

Crystal data: $C_{23}H_{18}N_2O_2Hg$, $M = 555.0$, monoclinic, $a = 9.8978(9)$, $b = 10.891(1)$, $c = 18.032(2)$ Å, $\beta = 96.41(1)°$, $U = 1931.6$ Å^3, space group $P2_1/c$, $Z = 4$, $D_c = 1.91$ g cm^{-3}, μ(Mo Kα) = 79.9 cm^{-1}, $F(000) = 1064$.

Data were measured at room temperature on a CAD4 automatic four-circle diffractometer in the range $2 \leq \theta \leq 24°$. 3422 reflections were collected, of which 2029 were unique with $I \geq 2\sigma(I)$. Data were corrected for Lorentz and polarization and also for absorption [33]. (Max. and min. absorption corrections: 1.269 and 0.723 respectively.) The structure was solved by Patterson methods and refined using the SHELX [34,35] suite of programs. In the final least squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions. Final residuals after eight cycles of least squares were $R = 0.0345$, $R_w = 0.0295$, for a weighting scheme of $w = 2.7899/[\sigma^2(F) + 0.000271(F)^2]$. Max. final shift/esd was 0.001. The max. and min. residual densities were 0.42 e Å^{-3} and −0.49 e Å^{-3} respectively. The asymmetric unit is shown in Fig. 1, along with the labelling scheme used in the text. Selected bond distances and angles, and final fractional atomic coordinates are given in Tables 1 and 3 respectively. Tables of anisotropic temperature factors, hydrogen atom positions and a complete listing of geometric data are available as supplementary data.

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References

[1] B.S. Jensen, *Acta Chem. Scand.*, *13* (1959) 1347; 1668; 1890.
[2] S. Miyazaki, H. Mukai, S. Umetani, S. Kihara and M. Matsui, *Inorg. Chem.*, *28* (1989) 3014, and references cited therein.
[3] C. Pettinari, F. Marchetti, A. Cingolani, C. Marciante, R. Spagna and M. Colapietro, *Polyhedron*, *13* (1994) 939.
[4] F. Bonati, L.A. Oro and M.T. Pinillos, *Polyhedron*, *4* (1985) 357.
[5] S. Saxena, R. Bohra and A.K. Rai, *Inorg. Chim. Acta*, *173* (1990) 191.
[6] C. Pettinari, G. Rafaini, C.G. Lobbia, A. Lorenzotti and B. Bovio, *J. Organomet. Chem.*, 405 (1991) 75.
[7] B. Bovio, A. Cingolani, F. Marchetti and C. Pettinari, *J. Organomet. Chem.*, *458* (1993) 39.
[8] C. Pettinari, F. Marchetti, D. Leonesi, M. Rossi and F. Caruso, *J. Organomet. Chem.*, *483* (1994) 123.
[9] M.F. Mahon, K.C. Molloy, B.A. Omotowa and M.A. Mesubi, *J. Organomet. Chem.*, *511* (1996) 227.
[10] R.G. Pearson, *J. Am. Chem. Soc.*, *85* (1963) 3533.
[11] R. Allmann, K. Flatau and H. Musso, *Chem. Ber.*, *105* (1972) 3067.
[12] K. Dietrich, H. Musso and R. Allman, *J. Organomet. Chem.*, *93* (1975) 15.
[13] R. Allmann and H. Musso, *Chem. Ber.*, *106* (1973) 3001.
[14] L.E. McCandlish and J.W. Macklin, *J. Organomet. Chem.*, *99* (1975) 31.
[15] P. Clare and F. Gockling, *Inorg. Chim. Acta*, *17* (1976) 229.
[16] R.J. Bertino and G.B. Deacon, *J. Organomet. Chem*, *67* (1974) C61.
[17] W. Depmeier, K. Dietrich, K. König, H. Musso and W. Weiss, *J. Organomet. Chem.*, *314* (1986) C1.
[18] K. Dietrich, K. König, G. Mattern and H. Musso, *Chem. Ber.*, *121* (1988) 1277.
[19] Y.M. Chow and D. Britton, *Acta Crystallogr. Sect. B*, *39* (1975) 1929.
[20] J.L. Wardell, in G. Wilkinson, F.G.A. Stone and E.W. Abel (eds.), *Comprehensive Organometallic Chemistry*, Pergamon, New York, 1982, Chapter 17, p. 863.
[21] D.L. Rabenstein, *Acc. Chem. Res.*, *11* (1978) 100.
[22] E. Buncel, R. Kumar and A.R. Norris, *Can. J. Chem.*, *64* (1986) 442.
[23] P.L. Goggin, R.J. Goodfellow, D.M. McEwan, A.J. Griffiths and K. Kessler, *J. Chem. Res. M.*, 2315 (1979).
[24] J.S. Casas, A. Castiñeiras, A. Sánchez, J. Sordo and E.M. Vázquez-López, *J. Organomet. Chem.*, *468* (1994) 1.
[25] R. Allmann, K. Flatau and H. Musso, *Chem. Ber.*, *105* (1972) 3067.
[26] R. Allmann and H. Musso, *Chem. Ber.*, *106* (1973) 3001.
[27] R. Allmann, K. Dietrich and H. Musso, *Justus Leibigs Ann. Chem.*, (1976) 1185.
[28] J.W. Sibert, S.J. Lange, C. Stern, B.M. Hoffman and A.G.M. Barrett, *J Chem. Soc. Chem. Commun.*, (1994) 1751.
[29] E.C. Okafor, *Polyhedron*, *2* (1983) 309.

[30] E.C. Okafor, *Spectrochim. Acta Part A:*, *37* (1981) 939.
[31] R.Kh. Freidlina, A.K. Kochetkov and A.N. Nesmeyanov, *Isvest. Akad. Nauk SSSR Otd. Khim. Nauk*, *445* (1948); *Chem. Abstr.*, (1950) 10569.
[32] M.S. Garcia Tasende, M.I. Suárez Gimeno, A. Sánchez, J.S. Casas and J. Sordo, *J. Organomet. Chem.*, *384* (1990) 19.
[33] N. Walker and D. Stewart, *Acta Crystallogr. Sect. A:*, *39* (1983) 158.
[34] G.M. Sheldrick, SHELX 86, *A Computer Program for Crystal Structure Determination*, University of Göttingen, 1986.
[35] G.M. Sheldrick, SHELX 76, *A Computer Program for Crystal Structure Determination*, University of Cambridge, 1976.