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VARIETY IN THE COORDINATION MODES OF β-DICARBONYL COMPOUNDS IN METAL COMPLEXES

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CONTENTS

ABBREVIATIONS

acacH	2,4-pentanedione (acetylacetone)
$acac^{3-}$	trianion of acetylacetone
bpy	2,2′-bipyridine

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bzacH	1-phenyl-1,3-butanedione (benzoylacetone)
dbmH	1,3-diphenyl-1,3-propanedione (dibenzoylmethane)
dpmH	2,2,6,6-tetramethyl-3,5-heptanedione (dipivaloylmethane)
etacH	ethyl 3-oxobutanoate (ethyl acetoacetate)
etmalH	diethyl malonate
hfacH	1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hexafluoroacetylacetone)
phen	1,10-phenanthroline
py	pyridine
tfacH	1,1,1-trifluoro-2,4-pentanedione (trifluoroacetylacetone)
ttaH	1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione (thenoyltrifluoroacetone)
β-dik (acac, etc.)	monoanion of a β-dicarbonyl compound working as an O,O′-chelating ligand or a counter anion in the outer sphere
β-dik–C (acac–C, etc.)	monoanion of a β-dicarbonyl compound bound to a metal atom through a carbon atom
β-dikH	neutral molecule of a β-dicarbonyl compound in general
β-dik–O (acac–O, etc.)	monoanion of a β-dicarbonyl compound working as an O-unidentate ligand
β-dik^{2-}	dianion of a β-dicarbonyl compound
η^3-acac, η^3-etac	monoanion of acacH or etacH bound to a metal atom through three carbon atoms in a trihapto fashion (η-allylic coordination mode)

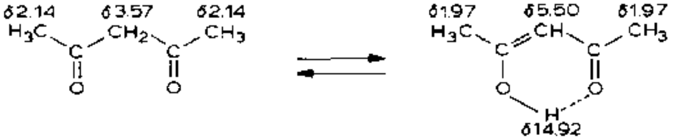
A. INTRODUCTION

2,4-Pentanedione (acetylacetone) and other β-dicarbonyl compounds constitute a class of the most important ligands which have been employed very widely from the outset of this century [1,2]. They are very versatile and exhibit a great variety of coordination modes besides the usual bidentate behavior of monoanions [3]. Although previous reviews were valuable in illustrating some coordination modes for these ligands [4–8], many novel modes have been explored since then. This review briefly summarizes the bonding modes established so far for β-dicarbonyl compounds as the molecule, monoanion, dianion and trianion, laying emphasis on the interconversion among them.

B. THREE COORDINATION MODES FOR NEUTRAL MOLECULES

(i) *Keto–enol tautomerism and the structures of enol molecules*

The β-dicarbonyl compound generally exists as an equilibrium mixture of the tautomeric keto and enol forms. The rate of spontaneous interconversion between these forms is rather slow at room temperature [9], and their simultaneous NMR spectroscopic observation is possible. For instance, the ^1H NMR spectrum of neat acacH is composed of OH, CH, CH_2, and CH_3 signals in accordance with the following equilibrium (δ in ppm from internal Me_4Si).



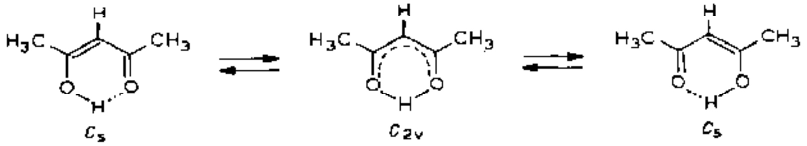
(1)

The equilibrium quotient $K = [\text{enol}]/[\text{keto}]$ for neat acacH is 3.59 (78.2% enol) at 37.3°C and decreases with rising temperature, ΔH and ΔS being -2.4 ± 0.2 kcal mol^{-1} and -5.2 ± 0.6 cal deg^{-1} mol^{-1}, respectively [10].

Replacement of the terminal methyl groups of acacH by an electron-withdrawing or aromatic group such as CF_3, C_4H_3S (2-thienyl), and C_6H_5 shifts the equilibrium in favor of the enol tautomer. Hexafluoroacetylacetone, thenoyltrifluoroacetone (in carbon disulfide), and dibenzoylmethane (in carbon tetrachloride), for example, exist entirely in the enol form [11]. Similarly the electron-withdrawing substituent at the central atom also increases the enol content; 3-chloro- and 3-ethoxycarbonyl-2,4-pentanedione are composed of 84 and 100% enol, respectively. On the other hand, the electron-releasing substituents decrease the enol content. Thus 3-methyl-, 3-ethyl- and 3-isopropyl-2,4-pentanedione contain 29, 28, and 0% enol at 25°C, respectively [12].

The enol tautomer is stabilized at least partially by the intramolecular hydrogen bond, and since the internally hydrogen-bonded molecule is less polar than the keto molecule, the enol form is favored by nonpolar solvents. Thus the enol content of acacH was reported to be 96, 95, 94 and 89% in carbon tetrachloride, diethyl ether, carbon disulfide, and benzene at 33°C, respectively [13]. In polar solvents, on the other hand, the fraction of keto molecules increases, the enol percent of acacH being 74, 67 and 62 in methanol, acetic acid, and dimethylsulfoxide, respectively, as compared with 81% for the neat liquid at the same temperature [13], and in water at 25°C, $K = [\text{enol}]/[\text{keto}]$ is as small as 0.13 [9].

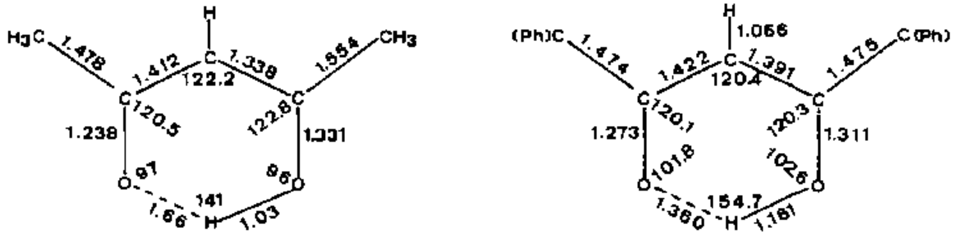
As is shown in eqn. (1), acacH exhibits only two methyl-proton signals at δ1.97 and δ2.14 assignable to the enol and keto methyls, respectively, indicating that the two methyl groups in an enol molecule are equivalent. The enol tautomer must either have the symmetric C_{2v} structure with a single energy minimum or exist in the asymmetric C_s forms with a low barrier to interconversion via the C_{2v} structure.



Acetylacetone is a liquid at room temperature (m.p. −23.2°C, b.p. 140.5°C) and has not been subjected to crystallographic examination. The electron diffraction study [14] revealed that 66 ± 5% of acacH vapor at 105°C exists in the enol form, and that the enol tautomer has the C_{2v} structure with a short linear and symmetric internal hydrogen bond; O–H = 1.19 Å and O ··· O′ = 2.381(20) Å. Bond lengths and angles in the hydrogen chelate ring are close to aromatic values; C–O = 1.315(7) Å, C–C = 1.416(10) Å, ∠OCC = 120.1(1.3)°, and ∠CCC = 118.0(2.5)°. The vapor molecule of hfacH was also reported [15] to have a planar C_{2v} structure with the O ··· O′ distance being 2.551(33) Å.

Recently Camerman et al. [16] crystallized a complex of diphenylhydantoin and 9-ethyladenine (antiepileptic drug) from acacH solution and found that one enol molecule of acacH per asymmetric unit is involved in the crystal lattice. X-ray analysis disclosed the structure of enol molecule in a rather isolated environment, since no contacts shorter than van der Waals distances were observed between acacH atoms and those of diphenylhydantoin and ethyladenine.

As is seen in Fig. 1, bond distances including the hydrogen bond are not symmetric, but are indicative of localized single and double bonds throughout the molecule. The O ··· O′ distance is 2.535 Å.



acacH

dbmH

Fig. 1. Bond lengths and angles for acetylacetone [16] and dibenzoylmethane [18] determined by X-ray and neutron diffraction methods, respectively.

The crystal structure of dibenzoylmethane has been determined by both X-ray [17] and neutron diffraction [18] methods. The intramolecular hydrogen bond is also asymmetric, the difference in O–H bond lengths being 0.199(17) Å [18]. The interatomic distances and angles within the enol ring are shown in Fig. 1. The O · · · O′ distance is 2.459(4) Å.

Similarly tetraacetylethane [19], 3,3-dithiobis(2,4-pentanedione) [20], 3,3′-trithiobis(2,4-pentanedione) [21], 2,2′-dithiobis(1-phenyl-1,3-butanedione) [22], and thenoyltrifluoroacetone [23] have also been reported to exist in the enol form which contains an asymmetric hydrogen bond. A neutron diffraction study on benzoylacetone [24] and X-ray studies on *p*-bromobenzoylacetone [25] and *p*-nitrobenzoylacetone [26] performed by Jones indicate that either molecule exists in the enol form and the intramolecular hydrogen bond is short with O · · · O′ being 2.489(5), 2.481(9) and 2.457(5) Å, respectively. However reliable evidence for asymmetry of the internal hydrogen bond was not obtained in these cases because of large thermal motion.

Thus enol molecules of β-dicarbonyl compounds have the asymmetric C_s structure in many cases. The symmetric C_{2v} structure observed for enol molecules of acacH and hfacH in the vapor state might be the result of statistical disorder. In fact inequivalence of the oxygen atoms in hfacH was indicated by X-ray photoelectron spectroscopy (XPS).

The O_{1s} ionization regions of malonaldehyde, hfacH and other related compounds were studied by XPS. Since these determinations are made on isolated gas-phase molecules on a time scale of 10^{-16} s, they may provide the experimental evidence for the molecular symmetry. All of these compounds show two dominant ionizations arising from oxygens, indicating that the two oxygen atoms are made inequivalent by virtue of an asymmetric hydrogen bond [27].

(ii) Metal complexes of neutral molecules

Various metal complexes containing a β-dicarbonyl compound as the neutral ligand have been isolated (Table 1), although they are not, in general, very stable. These complexes were prepared by three methods.

(a) Addition of a β-dikH molecule to a simple metal salt or a coordinatively unsaturated metal complex

$$MX_n + \beta\text{-dikH} \rightarrow MX_n(\beta\text{-dikH})$$

(b) Substitution of a weak neutral ligand with β-dikH

$$ML + \beta\text{-dikH} \rightarrow M(\beta\text{-dikH}) + L$$

(c) Addition of a proton onto an anionic β-diketonate ligand

$$M(\beta\text{-dik}) + HX \rightarrow MX(\beta\text{-dikH}) \text{ or } M(\beta\text{-dikH})^+ + X^-$$

TABLE 1

Isolated metal complexes containing a β-dicarbonyl compound as a neutral ligand

Complex	Method of preparation [a]	Coord. mode of β-dikH [b]	ν(CO) for β-dikH in Nujol	Ref.
$HgCl_2$(acacH)	(a)	(1)	1698, 1658	28
MoO_2Cl_2(acacH)	(a)	(1)	1695	29, 30
MoO_2Cl_2(etmalH)	(a)	(1)	1695	29
$MoOCl_3$(acacH)	(a)	(1)	1695, 1634	30
$SnCl_4$(acacH)	(a)	(1)	1731, 1670	31
$SnCl_4$(3-Me-acacH)	(a)	(1)	1673, 1613	31
$SnCl_4$(3,3-Me_2-acacH)	(a)	(1)	1680, 1607	31
$TiCl_4$(acacH)	(a)	(1)	1683, 1633	31
TiX_4(3,3-Me_2-acacH) (X = Cl, Br, I)	(a)	(1)	1680–1691, 1614–1621	31
$ZrCl_4$(3,3-Me_2-acacH)	(a)	(1)	1644, 1597	31
$CoBr_2$(acacH)	(a), (c)	(1)	1720sh, 1705	32
$CoCl_2$(acacH)	(a)	(1)	1727sh, 1703	33
$ZnCl_2$(acacH)	(a)	(1)	1715	33
$NiBr_2$(acacH)$_2$	(c)	(1)	1729sh, 1693	33, 34
$CrCl_2$(acac)(acacH)	(b)	(1)	1739sh, 1692	33
$CrBr_2$(acac)(acacH)	(c)	(1)	1680	33
$CoCl_2$(etacH)	(a)	(1)+(2)	1717sh, 1702, 1657	35
$CoBr_2$(etacH)	(a)	(1)+(2)	1720sh, 1703, 1685, 1650	35

$ZnCl_2$(etacH)	(a)	(1)+(2)	1730, 1706, 1625	35
$CoCl_2$(etmalH)	(a)	(1)+(2)	1750sh, 1729, 1698, 1657	35
$CoBr_2$(etmalH)	(a)	(1)+(2)	1755sh, 1726, 1690, 1655	35
$MnBr_2$(etmalH)	(a)	(1)+(2)	1753sh, 1726, 1658	35
$ZnCl_2$(etmalH)	(a)	(1)+(2)	1737, 1715, 1683sh, 1618	35
Eu(tta)$_3$(acacH)	(a)	(1)	1715	36
[Ni(acacH)$_3$](ClO$_4$)$_2$	(b)	(1)	1700	37
[Ni(acacH)$_2$(CH$_3$COOH)$_2$](ClO$_4$)$_2$	(b)	(1)	1700	37
[Ni(acacH)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$	(b), (c)	(1)	1700	37, 38, 39
[Mg(acacH)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$	(a)	(1)		40
[Zn(acacH)$_2$(H$_2$O)](ClO$_4$)$_2$	(b)	(1)+(2)	1725, 1700, 1620	41
[VO(ACOAP)(acacH)]·H$_2$O [c]	(a)	(1)	1700	42
[VO(ACAA)(acacH)(H$_2$O)]·H$_2$O [d]	(a)	(1)	1700	42
UO$_2$(acac)$_2$(acacH)	(a)	(2)	~1620	43, 44
MnBr$_2$(acacH)$_2$	(a)	(2)	1627	33, 45
[ReCl(acacH)(CO)$_3$]$_2$	(b)	(2)		46
[ReCl(bzacH)(CO)$_3$]$_2$	(b)	(2)	1590	46, 47
PtCl(acac)(acacH)	(c)	(3)	1627	49–52
Pt(PPh$_3$)$_2$(acacH)	(a)	(3)	1682	53
Pt(PPh$_3$)$_2$(etmalH)	(a)	(3)	1681	53

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[a] See section B(ii).

[b] (1) O,O′-chelation of a keto tautomer; (2) O-unidentate linkage of an enol form; (3) η^2(C,C′) coordination of an enol molecule.

[c] ACOAP–H$_2$ = $CH_3C(OH){=}CHC(CH_3){=}NC_6H_4OH(o)$.

[d] ACAA–H$_2$ = $CH_3C(OH){=}CHC(CH_3){=}NC_6H_4COOH(o)$.

In some cases, the central metal ion is reduced.

$$2\ MoOCl_3 + 3\ acacH \rightarrow 2\ MoOCl_2(acacH) + HCl + acacCl \qquad [30]$$

$$Co(acac)_3 + 2\ HBr + RH \rightarrow CoBr_2(acacH) + 2\ acacH + R\cdot \qquad [32]$$

There are three coordination modes proposed for β-dikH: (1) O,O′-chelation of a keto tautomer; (2) O-unidentate linkage of an enol form; and (3) η^2(C,C′) coordination of an enol molecule.

The tautomeric form of β-dikH is most conveniently diagnosed by infrared spectroscopy. The IR absorption bands in the regions of carbonyl and metal–oxygen stretching vibrations are especially helpful. Thus free acacH exhibits three carbonyl bands at 1730, 1712 and 1630 cm^{-1}. The higher frequency bands are attributed to the keto tautomer and the lowest-frequency band to enol.

(iii) O,O′-Chelation of the keto molecule

The majority of complexes listed in Table 1 show the ν(C=O) band at around 1700 cm^{-1} and are supposed to contain a ketonic acacH molecule as a chelating ligand. Only two compounds have been confirmed so far by X-ray analysis to have the proposed structure. A light green crystal of $NiBr_2(acacH)_2$ is composed of discrete octahedral molecules of the *trans* configuration, acacH molecules forming an O,O′-chelate ring of boat conformation [34].

The crystal structure of $[Ni(acacH)_2(H_2O)_2](ClO_4)_2$ was first reported by Anzenhofer and Hewitt [38] and reinvestigated later by Cramer et al. [39]. There are two non-equivalent, centrosymmetric cations per unit cell. In both cations the acacH ligand is coordinated in the keto form, but differs in the conformation of the six-membered chelate ring. In one cation, the ring system is nearly planar, but in the other it is folded in the boat conformation as was also found for $NiBr_2(acacH)_2$ [34]. Bond lengths and angles for the puckered cation are shown in Fig. 2.

(iv) O-Unidentate coordination of enol

Although $MnBr_2(acacH)_2$ has the same stoichiometry as $NiBr_2(acacH)_2$, their IR spectra are quite different. The bands observed for the former compound at 1627 and 1564 cm^{-1} must be assigned to the C⋯O and C⋯C stretching vibrations of the enol molecule [33].

X-ray analysis [45] revealed that the manganese(II) complex is composed of infinite $MnBr_2$ chains with acacH enol molecules occupying the axial coordination sites to complete the octahedral geometry of *trans*-$MnBr_4O_2$.

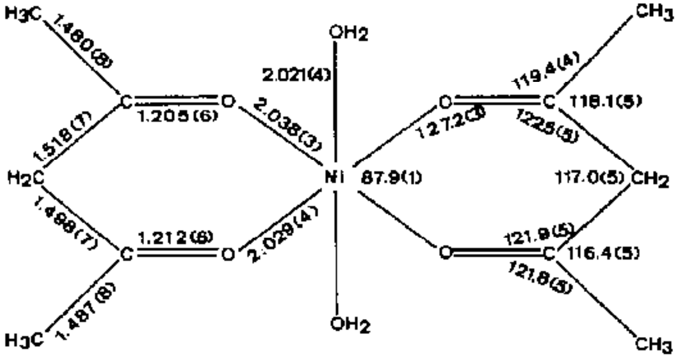


Fig. 2. Bond lengths and angles for the puckered cation in $[Ni(acacH)_2(H_2O)_2](ClO_4)_2$. Dihedral angles between the OCCO plane forming the bottom of the boat and the ONiO and CCC planes are 18.5° and 31.4°, respectively [39].

The acacH molecule is planar and coordinates to the metal atom through the carbonyl oxygen, holding the intramolecular hydrogen bond with the Mn–O and O · · · O′ distances being 2.20(2) and 2.56(3) Å, respectively.

Dimeric complexes $[ReCl(CO)_3(\beta\text{-dikH})]_2$ were obtained in the reactions of chloropentacarbonylrhenium(I) with acacH or bzacH in refluxing benzene [46]. The molecular structure of the bzacH complex determined by X-ray diffraction [47] is shown in Fig. 3. The two planar enol molecules are approximately at 90° to each of the Re–Cl bridges and are on the same side of the $ReCl_2Re$ plane.

Asymmetric internal hydrogen bonding in the coordinated bzacH is clearly indicated. The C=O, C–O and O · · · O′ distances, 1.29(2), 1.37(2) and 2.52(2) Å, respectively, correspond well to those values (1.288(5), 1.310(4) and 2.489(5) Å, respectively) for free bzacH determined by neutron diffraction [24].

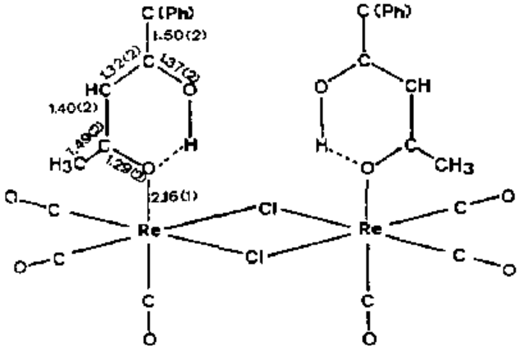
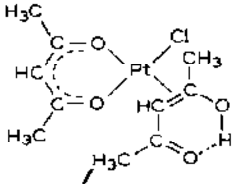


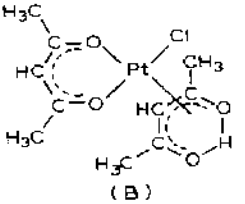
Fig. 3. Molecular structure of $[ReCl(CO)_3(bzacH)]_2$. The intramolecular O · · · O′ contact is 2.52(2) Å [47].

Involvement of the O-unidentate enol of acacH in $[ReCl(CO)_3(acacH)]_2$ [46] and $UO_2(acac)_2(acacH)$ [44] was inferred from the IR and ^1H NMR spectroscopy.

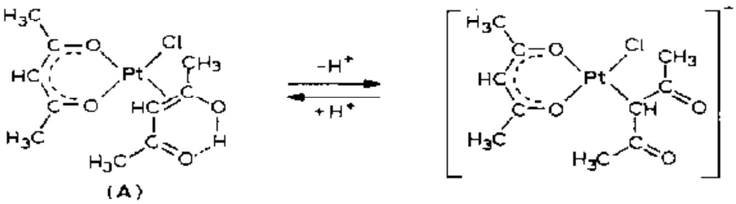
(v) $\eta^2(C,C')$-Coordination of enol

A platinum(II) complex, K[PtCl(acac)(acac–C^3)], which contains a central-carbon-bonded acac ligand [48], reacts with a strong acid to give a bright yellow precipitate PtCl(acac)(acacH). Lewis and co-workers investigated the structure by IR and NMR spectroscopy, and first proposed structure A in which an enol molecule of acacH coordinates to the metal in the η^2(C,C′) fashion [49], but later favored structure B in which the enol molecule is bonded as a delocalized π-system [50].


(A)


(B)

On the other hand, Behnke and Nakamoto supported structure A based on the detailed IR spectroscopic studies [51]. Preference for B by Gibson et al. [50] was based on the NMR equivalence of the methyl protons of the η-bonded acacH. However, Tsutsui and co-workers [52] showed that deprotonation of A to reproduce the carbon-bonded complex is reversible and rapid on the NMR time-scale in polar solvents, averaging the environments of methyl protons of the η^2-coordinated acacH.


(A)

Harvie and Kemmitt [53] obtained $Pt(PPh_3)_2(acacH)$ and $Pt(PPh_3)_2$-(etmalH) by the reactions of $Pt(PPh_3)_4$ with acacH and diethyl malonate, respectively, in refluxing benzene. Involvement of enol molecules was confirmed by IR and NMR data. These compounds may also have the η^2(C,C′) structure analogous to A.

C. COORDINATION MODES FOR MONOANIONS

Various coordination modes established so far for monoanions of β-dicarbonyl compounds are shown in Fig. 4.

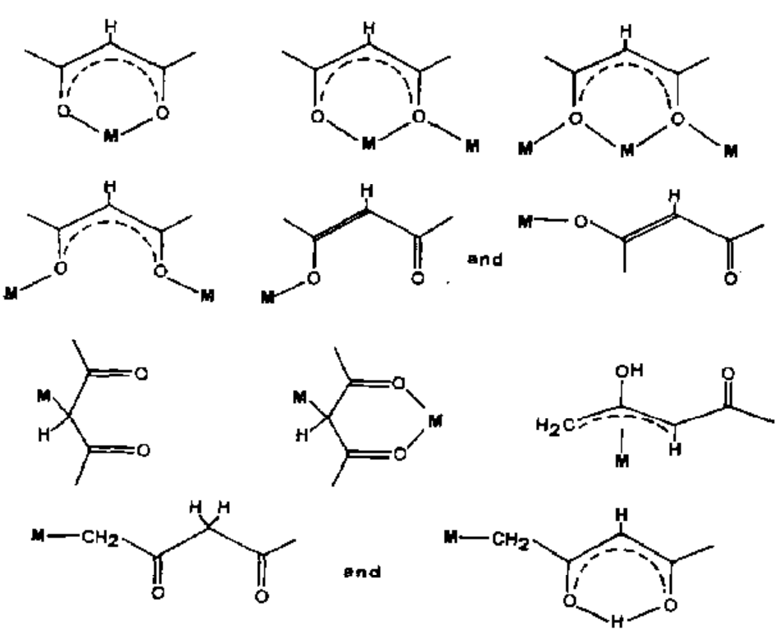


Fig. 4. Coordination modes for monoanions of β-dicarbonyl compounds in metal complexes.

(i) O,O′-Chelation and bridging

The O,O′-chelation is the most popular mode of coordination for the β-dik anions [54], and has been found for almost all of the metallic and metalloidal elements [3]. The oligomeric structures of some acac chelates of the first-row transition metals such as $[Mn(acac)_2]_3$ [55], $[Fe(acac)_2]_2$ [56a], $[Fe(acac)_2]_4$ [56b], $[Co(acac)_2]_4$ [57], $[Ni(acac)_2]_3$ [58], and $[Zn(acac)_2]_3$ [59] as well as $[Cd(acac)_2]_\infty$ [60] are well documented [5], in which one or both of the oxygen atoms of a chelating acac ligand are further linked to other metal atoms.

Besides these self-associated binary compounds, there have been reported many mixed-ligand dinuclear complexes including $Mn_2(acac)_4(CH_2{=}CHCH_2NH_2)_2$ [61], $M_2(acac)_4L$ (M = Co, Ni; L = py [58b], Ph_3AsO [62]), $Ni_2(acac)_4L_2$ (L = piperidine [58b], i-PrOH [63]), $Re_2(dbm)_2(CO)_6$ [64a], and $Os_3Rh(\mu\text{-}H)_2(acac)(CO)_{10}$ [64b], in which one of the oxygen atoms of the chelating β-dik ligand serves as the bridging donor atom.

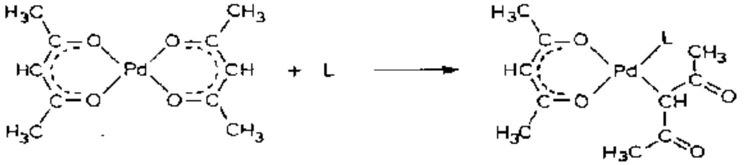
The purely bridging mode of coordination has sometimes been inferred for β-dik anions for example in $Re_6Me_{12}(tfac)_6$ [65] and $Nb_2Cl_3(dpm)_3$ [66], and was confirmed by X-ray analysis for two dpm ions in $Er_8O(OH)_{12}(dpm)_{10}$ [67].

(ii) Central carbon bonding

The central carbon bonding of β-dik was first found by Swallow and Truter in $Me_3Pt(acac\text{–}C^3)(bpy)$ [68]. $K[Pt(acac)_2Cl]$ was obtained by Werner in 1901 and supposed to involve an O-unidentate acac ligand, but X-ray analysis [69] as well as IR and NMR studies [70] revealed that the unidentate acac is bound to Pt through the central carbon. Since then various metal complexes containing the central-carbon-bonded β-dik ligands have been reported [6]; K[PtX(β-dik)(β-dik–C)] (β-dik = tfac and bzac; X = Cl and Br) [71], *fac*-$Mn(CO)_3$(LL)(β-dik–C) (β-dik = tfac and hfac; LL = bpy, phen and 2py) [72], AuL(β-dik–C) (β-dik = acac and bzac; L = PPh_3, $PEtPh_2$, PEt_3, P(*p*-tolyl)$_3$ and $AsPh_3$) [73], Hg(β-dik–C)$_2$ (β-dik = acac and dpm) [74], Ir(acac)$_2$(acac–C^3)L (L = NH_3, py, n-$PrNH_2$, and *p*-$MeC_6H_4NH_2$) [75], and (η-C_5Me_5)Ir(acac–C^3) [76].

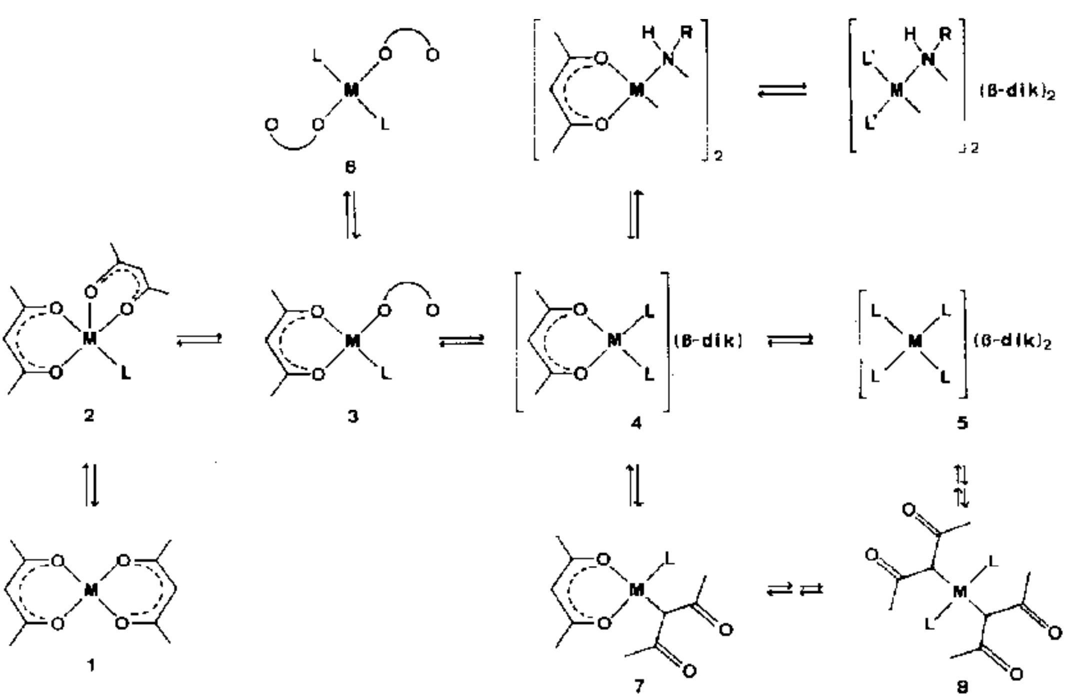
Although tetraacetylethane [19], 3,3′-dithiobis(2,4-pentanedione) [20], and 3,3′-trithiobis(2,4-pentanedione) [21] exist in the dienolic form (section B(i)), and the carbon-bonded hfac in $Mn(CO)_3(py)_2$(hfac–C^3) was suspected to be enol [72], the other compounds cited above contain β-dik of the keto form. Then the two oxygen atoms of the carbon-bonded β-dik ligand should be able to coordinate with another metal atom. In fact [Me_3Pt(β-dik)]$_2$ (β-dik = $C_3H_7COCHCOC_3H_7$ [77] and etac [78]) were the first examples of dinuclear complexes in which the β-dik anion serves as a C,O,O′-bridging ligand. Trinuclear complexes M[PtCl(acac)(acac–C^3)]$_2$ (M(II) = Mn, Fe, Co, Ni, Cu, Zn, Cd, Pd, VO, and UO_2) and the like were prepared [79] and characterized by IR [80] and NMR spectroscopy. The C,O,O′-bridging of β-dik in $Ir_2(acac)_6$ [75] and [(η-C_5Me_5)Rh(β-dik)]$_2$(PF_6)$_2$ (β-dik = acac, etac, and $CH_3COCHCOCH_2CH_2CH_3$) [76] was deduced from the IR and NMR data and confirmed by X-ray analysis for [(η-C_5Me_5)Rh(acac)]$_2$(BF_4)$_2$ [76].

Bis(acetylacetonato)palladium(II) was found by Baba et al. [81] in 1971 to react easily with Lewis bases (L) such as PPh_3, py and Et_2NH to afford Pd(acac)(acac–C^3)L in about 90% yields.



(2)

These were the first examples of the carbon-bonded complexes of acac with Pd(II) and their structures were determined by X-ray analysis [82,83]. This kind of reaction was successfully applied to Pt(acac)$_2$, Me_2Au(acac) and Pd(hfac)$_2$ to yield Pt(acac)(acac–C^3)L (L = PPh_3 [84], P(cyclohexyl)$_3$ [84] and py [85]), Pt(acac–C^3)$_2$(py)$_2$ [85], Me_2Au(acac–C^3)(PMe_2Ph) [86] and Pd(hfac)(hfac–C^3)L (L = Me_2NH and other bases (see below)) [87], respectively.



Scheme I.

The reaction of etacH with $Na_2[PdCl_4]$ in aqueous alkaline solution gave a yellow unidentified intermediate with the formula $Pd(etac)_2 \cdot 0.5H_2O$, which in dichloromethane turned spontaneously into the bis(O,O′)-chelate, $Pd(etac)_2$. On the other hand, the intermediate reacted with excess amounts of nitrogen bases (L) in appropriate solvents to afford the central-carbon-bonded complexes $Pd(etac\text{–}C^2)_2L_2$ (L = py, 2-Me-py, $PhCH_2NH_2$ and n-$BuNH_2$) [88]. The molecular structure of *trans*-$Pd(etac\text{–}C^2)_2(2\text{-Me-py})_2$ was determined by X-ray analysis [89]. In a similar fashion, Newkome et al. [90] prepared interesting Pd(II) complexes with tridentate and tetradentate ligands involving two β-dik moieties which are central-carbon-bonded to Pd at mutually *trans* and *cis* positions, respectively, the latter exhibiting antitumor activity.

In recent years Okeya et al. have studied extensively the reactions of binary and mixed-ligand bis(β-diketonato)palladium(II) and -platinum(II) chelates [91] with various nitrogen bases [92–94] and tertiary phosphines [95]. Many types of complexes have been obtained depending on the natures of central metals, β-dik ligands and the attacking Lewis bases, and the possible reaction routes are shown in Scheme I.

For example, when a mixture of $Pd(acac)_2$ (**1a**) and Et_2NH was warmed to result in a clear solution and then kept in a refrigerator overnight, $[Pd(acac)(Et_2NH)_2](acac)$ (**4a**) was obtained in a 66% yield [92]. On the contrary, when the solution was kept at room temperature to let the excess amine evaporate spontaneously, Pd(acac)(acac–C^3)(Et_2NH) (**7a**) was left in an 81% yield [81]. When complex **1a** was allowed to react with excess Et_2NH in solution, the absorption spectrum changed with time, exhibiting distinct isosbestic points to reach the spectrum of authentic **4a** [96].

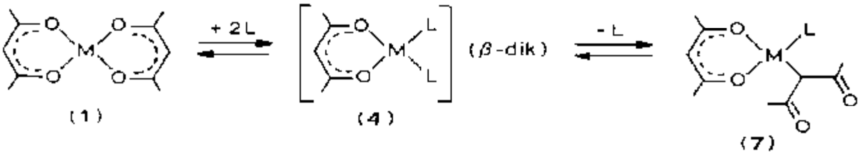
$$\underset{\mathbf{1a}}{\mathrm{Pd(acac)_2}} + 2\ \mathrm{Et_2NH} \rightarrow \underset{\mathbf{4a}}{\left[\mathrm{Pd(acac)(Et_2NH)_2}\right]}\mathrm{(acac)} \qquad (3)$$

The second order rate constant of this reaction at 25°C was 8.27×10^{-2}, 1.14×10^{-3}, and 9.4×10^{-4} $dm^3\ mol^{-1}\ s^{-1}$ in methanol, tetrahydrofuran and benzene, respectively. Complex **7a** also reacted with Et_2NH to afford **4a** (eqn. (4)), but the rate (9.70×10^{-4} $dm^3\ mol^{-1}\ s^{-1}$ in methanol at 25°C) was two orders of magnitude smaller than that for the overall reaction [96].

$$\underset{\mathbf{7a}}{\mathrm{Pd(acac)(acac{-}C^3)(Et_2NH)}} + \mathrm{Et_2NH} \rightleftarrows \underset{\mathbf{4a}}{\left[\mathrm{Pd(acac)(Et_2NH)_2}\right]}\mathrm{(acac)} \qquad (4)$$

These preparative and kinetic results indicate that complex **7a** is not produced directly from **1a** as an intermediate for **4a**, but is derived conversely via **4a**. The equilibrium constant of reaction (3) was determined to be 3.93×10^6 and 32.9 $dm^6\ mol^{-2}$ in methanol and dichloromethane, respectively, at 25°C [96]. In methanol the salt-like complex **4a** is quite stable and complex **7a** is not involved at all in the equilibrium mixture. In dichloromethane, on the other hand, the equilibrium constant of reaction (4) is 0.224 $dm^3\ mol^{-1}$ at 25°C and **4a** is readily converted into **7a**.

In the case of two-coordinate Hg(II) complex of 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione, an intramolecular mechanism was proposed by Fish [97] for the linkage isomerization between the O-unidentate and C-unidentate states. In the present case, the rearrangement of the chelating acac to the central-carbon-bonded state induced by the reaction of Et_2NH with **1a** occurs by the following consecutive replacement mechanism



The nucleophilic attack of β-dik as a carbanion not only on the unsaturated ligands such as olefin [98], imine [99], and cyanide [100], but also on the metal atoms, for example, in $Me_3PtI(bpy)$ [101], $PtBr_2$(1,5-hexadiene) [102], $Mn(CO)_4(LL)$ (LL = bpy, phen and 2py) [72], and (η-C_5Me_5)-IrCl(acac) [76] has been well documented. In the presence of appropriate ancillary ligands, metal atoms prefer the carbon bonding to the oxygen bonding when they accept a β-dik anion as a unidentate ligand.

The tendency of a β-dik anion to form the central carbon bond is parallel with the preference of the keto tautomer over enol [11]. Thus Pd(etac)$_2$ reacts with excess pyridine to give Pd(etac–C^2)$_2$(py)$_2$, whereas **1a** yields only Pd(acac)(acac–C^3)(py) [92]. Ito and Yamamoto [103] examined the ligand substitution reactions of Pt(acac)(acac–C^3)(PPh$_3$) with several β-dikH in refluxing toluene and found that the keto-favoring β-dikH selectively replaces the carbon-bonded acac, while the enol-favoring β-dikH substitutes the chelating acac.

However, even the hfac anion can realize the central carbon bonding in some cases. Thus Pd(hfac)(hfac–C^3)L complexes with 2,6-dimethyl-, 3,5-dimethyl- and 2,4,6-trimethylanilines [93] as well as dimethylamine, 2,6-dimethylpyridine, phenoxathiin and phenazine [87] as L have been prepared. Recently *cis*- and *trans*-PtCl$_2$(Et$_2$S)$_2$ were reported to react with Tl(β-dik) in methanol at room temperature to afford Pt(β-dik)(β-dik–C^3)(Et$_2$S) (β-dik = acac, tfac and hfac) [104].

(iii) Outer-sphere coordination

Readiness of the reaction between M(β-dik)$_2$ and Lewis bases (L) depends upon the basicities of both the β-dik anion and L, being in the sequence hfac > tfac > bzac ~ acac and alkylamines > benzylamine > pyridine. Reactions of M(acac)(β-dik) (β-dik = tfac and hfac) with L to afford complexes **4** (Scheme I) demonstrate this trend, displacing tfac and hfac preferentially into the outer sphere. Although pyridine reacts with Pt(tfac)$_2$ to give [Pt(py)$_4$](tfac)$_2$, less basic 4-cyanopyridine cannot displace tfac, but removes hfac in Pt(hfac)$_2$ [94].

Similarly aniline and its derivatives, which are less basic than alkylamines and pyridine, cannot substitute β-dik such as acac, bzac and tfac in Pd(β-dik)$_2$ at room temperature, but react with Pd(hfac)$_2$ to give complexes **7**, **4**, and **5** depending on the reactants' mole ratio [93]. In refluxing benzene, however, anilines react with various Pd(β-dik)$_2$ to give rise to the anilide bridged dinuclear complexes [Pd(β-dik)(anilido)]$_2$ [93].

Steric demand of Lewis base ligands L also exerts an important influence on the relative stabilities of the mixed ligand complexes. In general primary amines and pyridine displace both of the β-dik ligands in M(β-dik)$_2$ to afford complexes **5**, whereas secondary amines give only complexes **4**. Tertiary amines do not react with M(β-dik)$_2$ to yield complexes **4**. Tribenzylamine and 2,6-diphenylpyridine did react with Pd(hfac)$_2$, but the products were orthometallated complexes [92]. Siedle [105] succeeded in characterizing in situ at lower temperatures the intermediates containing a unidentate hfac ligand in the orthometallation reactions of Pd(hfac)$_2$ with *N*,*N*-dimethylbenzylamine and methylbenzyl sulfide.

A large number of complexes **4** and **5** have been prepared [92–95,106,107]. In spite of their salt-like compositions, most of them are not soluble in water, but dissolve in aprotic solvents retaining the tight ion-pair structures as evidenced by the molecular weight determinations. The crystal structure of $[Pd(acac)(Et_2NH)_2](acac)$ (**4a**) at −170°C was determined by Kasai and co-workers [108]. The acac plane in the outer sphere stands aside of the coordination plane sharing a common C_2 axis with the dihedral angle of 80.8°. The cation and the anion are bound together by hydrogen bonds between the coordinated amine molecules and the carbonyl oxygens of the acac anion in the outer sphere, and the interaction persists in solution. The ^1H NMR data give the relative strength of the hydrogen bonds in the sequence bzac > acac > tfac > hfac [92] in accordance with the basicity sequence of β-dik anions [109]. The amine protons are deuterated by $CDCl_3$ and the rate is also parallel with the basicity of β-dik in the outer sphere. A mechanism assuming the alkylamido complex as an intermediate has been proposed [92,110].

(iv) O-Unidentate linkage

Since the carbon-bonded complex **7** does not intervene between complexes **1** and **4**, the intermediate of reaction (3) must be a complex of type **3** containing an O-unidentate β-dik ligand. In fact the NMR monitoring disclosed that $Pt(tfac)_2$ reacts with an equimolar amount of PPh_3 to produce $Pt(tfac)(tfac{-}O)(PPh_3)$ exclusively, which is converted into $[Pt(tfac)(PPh_3)_2](tfac)$ by the reaction with another equivalent of PPh_3 [95]. Although the above O-bonded complex was not isolated and $Pd(acac)(acac{-}O)(Et_2NH)$, the expected intermediate in reaction (3), could not even be detected spectroscopically [96], many compounds containing the β-dik anion as an O-unidentate ligand have been prepared. The first examples were $Me_2Si(acac{-}O)_2$ and $Me_3Si(acac{-}O)$ [111] followed by $Hg(\beta\text{-dik}{-}O)_2$ (β-dik = acac, dpm, and 2,6-dimethyl-3,5-heptanedionate) [112], $Pt(acac{-}O)_2L_2$ ($L = PEt_3$ [113] and piperidine [114]), $Pt(acac)(acac{-}O)\{P(o\text{-tolyl})_3\}$ [95], $Cu(acac)(hfac{-}O)(phen)$ [115], and $M(CO)_5\{PPh(acac{-}O)_2\}$ (M = Cr and W) [116].

The central-carbon-bonding of β-dik is more favorable for Pd(II) than Pt(II) and the reverse is true as preference for the O-unidentate linkage. Thus $Pd(acac)_2$ reacts with PEt_3 to give $Pd(acac)(acac{-}C^3)(PEt_3)$ exclusively [95], whereas $Pt(acac)_2$ results only in $Pt(acac{-}O)_2(PEt_3)_2$ [113]. In the reactions of $M(acac)_2$ with secondary amines, Pd(II) gives complexes **4** and **7** [92], while Pt(II) gives **4** and **6**, e.g., a pair of linkage isomers $[Pt(acac)(piperidine)_2](acac)$ and $Pt(acac{-}O)_2(piperidine)_2$ [94]. On the other hand, the reactions of piperidine with $Pt(tfac)_2$ and $Pt(hfac)_2$ give only **6** and **4**, respectively [94]. Thus preference for the O-unidentate bonding by β-dik is in the sequence tfac > acac > hfac.

The O-unidentate acac anions involved in the trialkylsilyl compounds are a mixture of *cis* and *trans* isomers with respect to the C=C bond, and the *cis* isomer undergoes rapid intramolecular head-to-tail rearrangement, whereas the *trans* isomer is stereochemically rigid [117]. On the contrary, the acac anions involved in the above-mentioned Pt(II) complexes have the *cis* configuration exclusively, but show no fluxional motion at room temperature [94,113]. The *cis* configuration of the unidentate β-dik ligands in Cu(acac)(hfac–O)(phen) [115] and $Cr(CO)_5\{PPh(acac\text{–}O)_2\}$ [116] was confirmed by X-ray analysis.

The O-unidentate bonding of tfac seems to be much more stable than that of symmetric β-ketoenolates and a number of complexes have been obtained [94,95]: M(tfac)(tfac–O)L (M = Pd and Pt, L = $P(o\text{-tolyl})_3$; M = Pd, L = $P(cyclohexyl)_3$), M(acac)(tfac–O)L (M = Pd and Pt, L = $P(o\text{-tolyl})_3$; M = Pt, L = PPh_3 and PEt_3), $Pt(tfac\text{–}O)_2L_2$ (L = PEt_3, $P(cyclohexyl)_3$, Et_2NH and piperidine), and $Pt(acac\text{–}O)(tfac\text{–}O)(PEt_3)_2$. Kinetic and equilibrium studies [118] showed that the reaction

$$Pd(tfac)_2 + P(o\text{-tolyl})_3 \rightleftarrows Pd(tfac)(tfac\text{-O})\{P(O\text{-tolyl})_3\}$$

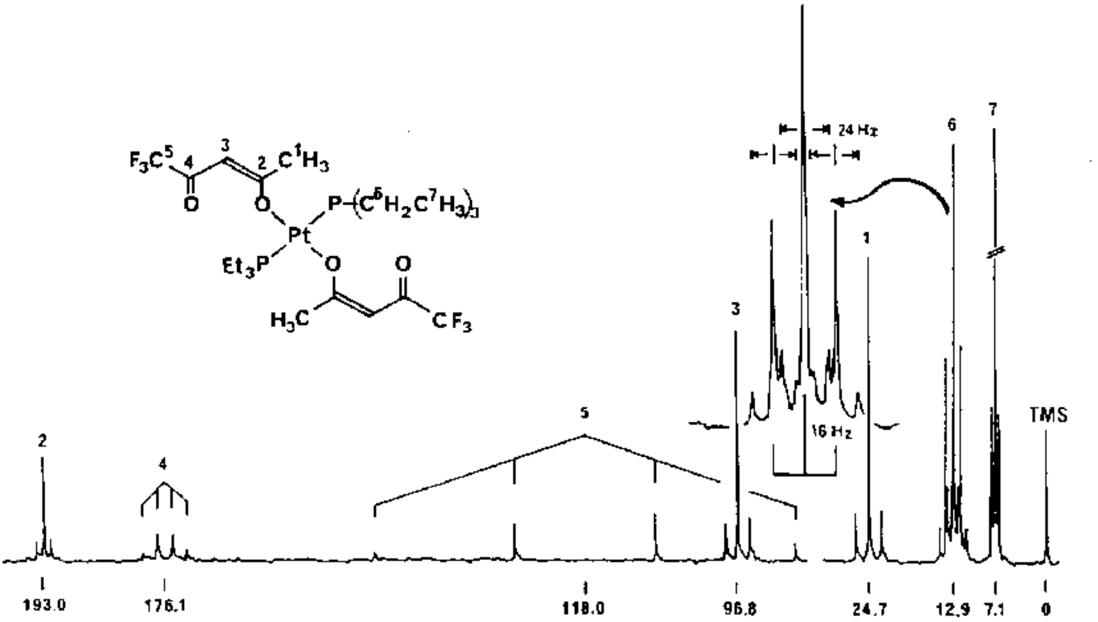


Fig. 5. $^{13}C\{^1H\}$ NMR spectrum at 15.04 MHz of $Pt(tfac\text{–}O)_2(PEt_3)_2$ in $CDCl_3$ [95]. The J(Pt–C) values are 55, 28 and 55 Hz for CH_3, CO and CH of tfac, and 24 and 15 Hz for CH_2 and CH_3 of PEt_3, respectively. ^1J(C–F) = 292 Hz and ^2J(C–F) = 31 Hz.

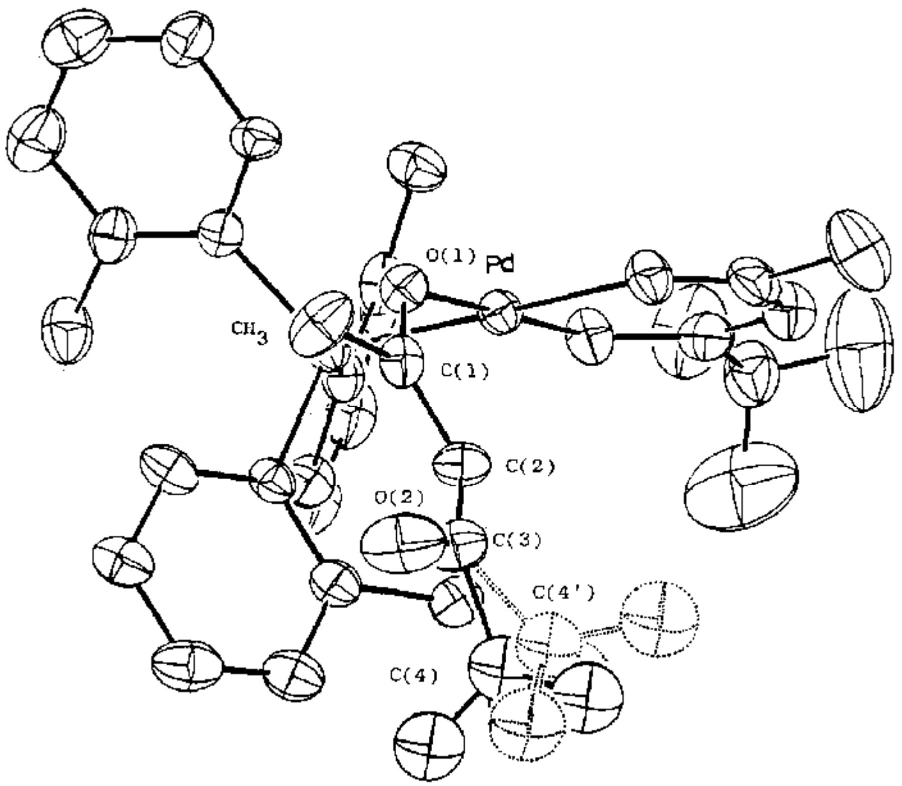


Fig. 6. ORTEP drawing of Pd(tfac)(tfac–O){P(*o*-tolyl)$_3$} involving the disordered CF$_3$ group [119].

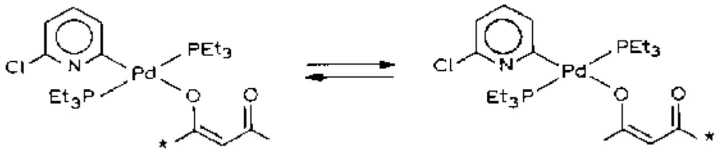
is reversible and the equilibrium constant was obtained as 1.38×10^3, 4.35×10^3, and larger than 10^9 dm^3 mol^{-1} at 25°C in benzene, dichloromethane and methanol, respectively. The steric requirements of P(*o*-tolyl)$_3$ seem to prevent formation of [Pd(tfac){P(*o*-tolyl)$_3$}$_2$](tfac) and Pd(tfac)-(tfac–C^3){P(*o*-tolyl)$_3$}.

The ^{1}H and ^{13}C NMR data indicate that the unidentate tfac anions in these complexes are bound to the metal atom through the acetyl oxygen [95]. For example the ^{13}C{^{1}H} spectrum of Pt(tfac–O)$_2$(PEt$_3$)$_2$ shown in Fig. 5 is compatible with the proposed structure.

X-ray analysis of Pd(tfac)(tfac–O){P(*o*-tolyl)$_3$} (**3a**) confirmed the acetyl–oxygen bonding of the unidentate tfac to Pd (Fig. 6). The dangling CF$_3$CO group is positioned *trans* to the bonding oxygen atom around the C=C bond, the torsion angle between the C(1)–CH$_3$ and C(3)–O(2) bonds being 1.1° [119]. This geometrical structure is not consistent with the NMR data indicating that the O-unidentate tfac ligand has primarily the *cis* configuration in CDCl$_3$ [95].

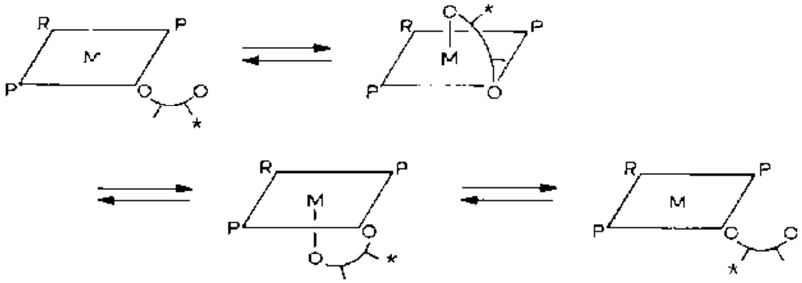
Recently palladium(II) complexes of the Pd(β-dik–O)(pyridyl)(PEt$_3$)$_2$

type containing an O-unidentate acac, tfac, or hfac anion and a 2-, 3-, 4-pyridyl or 6-chloro-2-pyridyl group as ligands were prepared and characterized mainly by ^1H and ^{13}C NMR spectroscopy [120]. The acac and hfac ligands in the Pd(β-dik–O)(C_5H_3(6-Cl)N–C^2)(PEt_3)$_2$ complexes undergo the head-to-tail intramolecular donor-atom exchange.



(5)

The NMR studies indicate that the dangling acetyl group of the acac ligand is positioned *cis* to the coordinating oxygen atom with respect to the C=C bond. As a mechanism for reaction (5) a simple oscillatory motion of the β-diketonate ligand spanning the apical and basal coordination sites in the square-pyramidal intermediate is proposed (eqn. (6)) [120]



(6)

Five-coordinate complexes of d^8 metals are believed to be involved as intermediates in ligand substitution [121] and some *cis–trans* isomerization [122] reactions, but they have scarcely been isolated. The reactions of Pd(hfac)$_2$ with an equimolar amount of P(*o*-tolyl)$_3$ in n-hexane at room temperature gave Pd(hfac)$_2${P(*o*-tolyl)$_3$} (**2a**) in 85% yield. Similarly Pt(hfac)$_2${P(*o*-tolyl)$_3$} (**2b**) and Pt(hfac)$_2${P(cyclohexyl)$_3$} (**2c**) were also obtained in 89 and 93% yields, respectively. The molecular structures of **2a** and **2c** were determined by X-ray analysis [123] and the former is shown in Fig. 7. The ^1H, ^{13}C and ^{19}F NMR studies indicate that these complexes are stereochemically rigid in CD_2Cl_2 at $-50°C$ but are fluxional at room temperature. Two kinds of twist modes were proposed as the mechanism for the intramolecular coordination-site exchange [123].

An analogous compound Pd(hfac)$_2$(PPh$_3$) [124a] and the complex cations in [Pd(hfac)(triphos)]BPh$_4$ (triphos = $Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2$) [124b] were also shown by X-ray analysis to have similar distorted square-pyramidal structures. They are also fluxional in solution. The activation parameters for the coordination-site exchange reactions of Pd(hfac)$_2${P(*o*-tolyl)$_3$} and [Pd(hfac)(triphos)]$^+$ measured by ^{19}F NMR line shape analysis

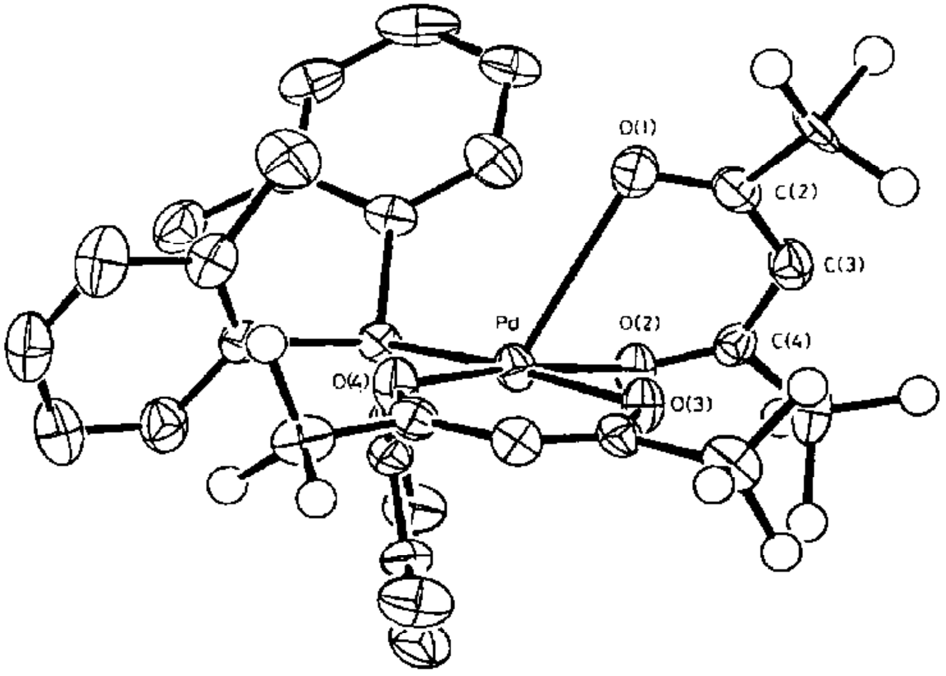


Fig. 7. The molecular structure of Pd(hfac)$_2${P(*o*-tolyl)$_3$} [123]. Pd–O(1) = 2.797(6) Å, Pd–O(2) = 2.017(5) Å and ∠O(1)PdO(2) = 76.0(2)°.

are $\Delta H^* = 7.7 \pm 1$ and 8.1 ± 1 kcal mol^{-1}, and $\Delta S^* = -20 \pm 5$ and -21 ± 3 cal deg^{-1} mol^{-1}, respectively [124].

(v) η-Allylic coordination

Sodium tetrachloropalladate(II) was found by Tezuka et al. [125] to catalyze the ethanolysis of diketene to furnish etacH, and yellow crystals separated at the end of the reaction were identified as [PdCl(η^3-etac)]$_2$ (**9b**) and their structure was determined by X-ray analysis [126]. Similar catalytic solvolysis of diketene in water [127] and acetone [128] to produce acetoacetic acid and 2,2,6-trimethyl-4H-1,3-dioxin-4-one, respectively, gave rise to η-allylic Pd(II) complexes of the products. Complex **9b** was also prepared by the direct reaction between PdCl$_2$ and etacH in water at 70°C in an 85% yield [125,129].

The molecular structure of **9b** resembles that of [PdCl(η-allyl)]$_2$ [130], the dihedral angle between the Pd(μ-Cl)$_2$Pd plane and the η^3-etac plane being 108° [126]. In a crystal the dimeric molecule is connected with adjacent molecules by the intermolecular hydrogen bonds. In CDCl$_3$ solution the intermolecular hydrogen bonds are broken and instead the intramolecular hydrogen bond is maintained, and the ^{1}H NMR spectrum shown in Fig. 8 is well interpreted based on the proposed structure [129].

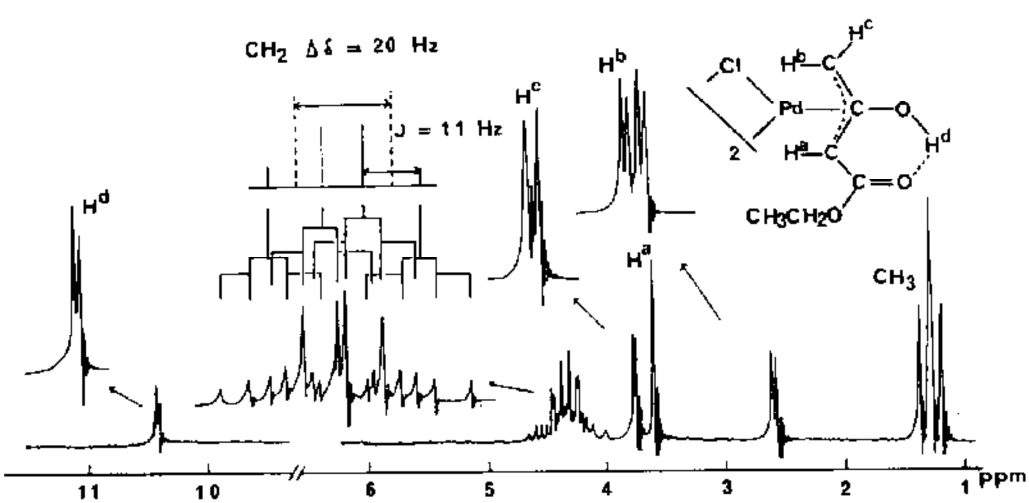
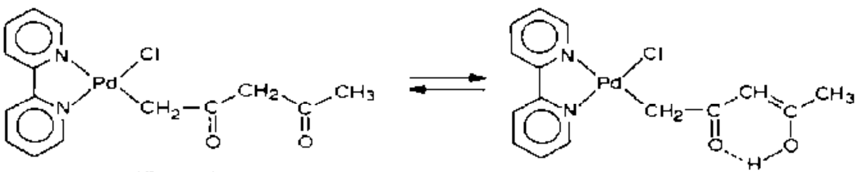


Fig. 8. ^{1}H NMR spectrum of $[PdCl(\eta^3\text{-etac})]_2$ in $CDCl_3$ [129]. $J(bc) = 3.4$ Hz, $J(bd) = 1.2$ Hz, and $J(CH_3-CH_2) = 9.2$ Hz.

The reaction of $PdCl_2(PhCN)_2$ with acacH in acetone gave $[PdCl(acac)]_2$ at 0°C and $[PdCl(\eta^3\text{-acac})]_2$ (**9a**) at room temperature. By means of the bridge-splitting reactions, these insoluble compounds were converted into the soluble mononuclear ones PdCl(acac)L and $PdCl(\eta^3\text{-acac})L$ ($L = PPh_3$ and $AsPh_3$), respectively [131]. They constitute two pairs of linkage isomers of a novel type.

(vi) Terminal carbon bonding

Complex **9b** reacts with py, bpy, and their derivatives in benzene to afford mononuclear complexes $PdCl(CH_2COCH_2COOEt)L_2$ containing the terminal-carbon-bonded β-ketoester [132]. The molecular structure of *cis*-$PdCl(CH_2COCH_2COOCH_2Ph)(py)_2$was determined by X-ray analysis [133]. In a similar way, complex **9a** reacts with bpy and other bidentate ligands in chloroform to give $PdCl(CH_2COCH_2COCH_3)(bpy)$, etc. (**10a**). Although the terminal-carbon-bonded β-ketoester in the corresponding complex $PdCl(CH_2COCH_2COOEt)(bpy)$ (**10b**) is keto exclusively, complex **10a** is a mixture of keto and enol tautomers with the equilibrium quotient $K = [enol]/[keto] = 0.7$ in $CDCl_3$ at 25°C [131].



10a-keto 10a-enol

Unsubstituted acacH favors the enol form, *K* being 6.7 in chloroform at 33°C [13]. The present result indicates that the {(bpy)ClPdCH$_2$} moiety in **10a** serves as an electron-releasing substituent on acacH.

D. COORDINATION MODES FOR DIANIONS

There are seven coordination modes for dianions of β-dicarbonyl compounds, which are shown in Fig. 9. Most of them were found rather recently.

(i) Central carbon bonding and chelation through terminal carbons

3,3-Di-μ-selenobis(2,4-pentanedione) was prepared by the reaction of SeCl$_4$ with acacH and its diselenacyclobutane structure with four acetyl groups was inferred from the IR and NMR spectra [134]. Dichloro(2,4-pentanedionato^{2-}–C^1,C^5)tellurium(IV) was obtained from the reaction of TeCl$_4$ with acacH and reduced with aqueous NaHSO$_3$ to afford 2,4-pentanedionato^{2-}–C^1,C^5-tellurium(II). The C,C-chelated structures of these complexes were deduced on the basis of spectroscopic data [134] and ascertained by X-ray analysis [135]. The molecular structures of 1,3-dimethyl-, 1,5-dimethyl-, 3,3-dimethyl- and 1,3,5-trimethyl-2,4-pentanedionato^{2-}–C^1,C^5-tellurium(II) were also determined [136].

(ii) Dienediolate chelation

Dicarbonyl(η-cyclopentadienyl)(phenyldichlorophosphane)manganese reacted with neat acacH in the presence of Et$_3$N to give (η-C$_5$H$_5$)(CO)$_2$Mn-

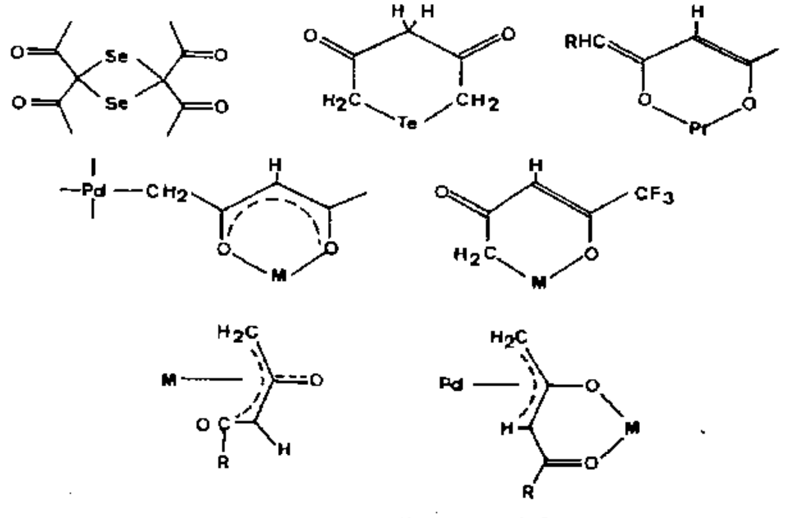
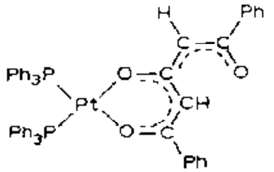


Fig. 9. Coordination modes for dianions of β-dicarbonyl compounds in metal complexes.

$\{\mathrm{Ph\overline{POC(=CH_2)CH{=}C(CH_3)O}}\}$, whose structure was determined by X-ray to reveal that the $acac^{2-}$ ion forms the dienediolate chelate with the phosphorus atom [137]. Similarly, reactions of $\mathrm{(CO)_5M(PPhCl_2)}$ with acacH in the presence of $\mathrm{Et_3N}$ gave $\mathrm{(CO)_5M\{Ph\overline{POC(=CH_2)CH{=}C(CH_3)O}\}}$ (M = Cr and W), the structure of the Cr(0) complex being determined by X-ray analysis [116].

Very recently Kemmitt and co-workers [138] obtained the first example of a transition metal complex in which a β-dicarbonyl ligand is chelating as a dienediolate dianion. Thus 1,5-diphenyl-1,3,5-pentanetrione reacted with $\mathrm{PtCO_3(PPh_3)_2}$ in warm ethanol to afford $\mathrm{\overline{Pt\{OC(CHCOPh)CHC(Ph)}}$-$\mathrm{\overline{O}\}(PPh_3)_2}$ which was characterized by X-ray crystallography.



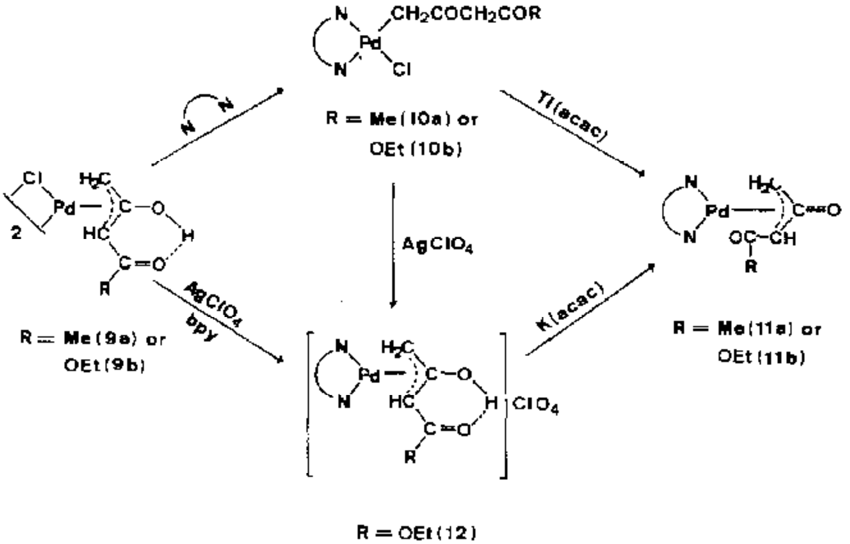
The six-membered chelate ring is essentially planar, the C–C and C–O bond lengths indicating the usual electron delocalization. The CHC(Ph)O substituent is also planar and the C–C and C–O bond distances are indicative of a highly conjugated system [138].

(iii) C,O,O′-Bridging

As was noticed previously in section C(vi), $\mathrm{PdCl(CH_2COCH_2COCH_3)}$-(bpy) (**10a**, HY) still has an ionizable hydrogen and reacted with $\mathrm{Cu(acac)_2}$, $\mathrm{VO(acac)_2}$ and $\mathrm{Pd(acac)_2}$ to afford insoluble trinuclear complexes $\mathrm{CuY_2}$, $\mathrm{VOY_2}$ and $\mathrm{PdY_2}$. Similar reactions of **10a** with excess $\mathrm{Be(acac)_2}$, $\mathrm{Pd(acac)_2}$ and $\mathrm{Pd(tfac)_2}$ to replace only one of the chelating ligands gave soluble dinuclear complexes M(β-dik)Y. The ligand substitution reactions of $\mathrm{[Cu(acac)(bpy)]ClO_4}$ and [Pd(hfac)(bpy)](hfac) with **10a** also produced $\mathrm{[CuY(bpy)]ClO_4}$ and [PdY(bpy)](hfac), respectively. In these complexes the $acac^{2-}$ ligand is bound to a Pd atom through the terminal carbon and chelates another metal atom with two oxygen atoms [139].

(iv) η-Allylic coordination

Complexes **10a** and **10b** were treated with Tl(acac) in benzene and dichloromethane, respectively, at room temperature. Contrary to expectation, the acac ion was not coordinated with Pd in place of the chloride ligand, but acted as a base to accept a proton from the terminal-carbon-bonded β-dik ligand in **10a** and **10b**, resulting in novel trihapto complexes of $\beta\text{-dik}^{2-}$ ions, $\mathrm{Pd}(\eta^3\text{-acac}^{2-})\mathrm{(bpy)}$ (**11a**) and $\mathrm{Pd}(\eta^3\text{-etac}^{2-})\mathrm{(bpy)}$ (**11b**) in 93



Scheme II.

and 97% yields, respectively [129]. As is indicated in Scheme II, complex **11b** was also derived from **9b** via another route. The bridging chloride in **9b** was first displaced by reaction with $AgClO_4$ in acetone; ligand bpy was then added to give $[Pd(\eta^3\text{-etac})(bpy)]ClO_4$ (**12**), which retains the η^3 structure of the etac monoanion. Several bases were examined and K(acac) was the best in abstracting the enolic proton in **12** to produce complex **11b**. The yield of **11b** from **9b** via this route was also excellent (95%) [129].

Figure 10 exemplifies the ^1H NMR spectrum of **11b**, which is much simpler than that of **9b** shown in Fig. 8. In the case of **9b** the ethoxycarbonyl group is held at the *syn* position by virtue of intramolecular hydrogen bonding. The diastereotopic methylene protons exhibit the 16-line multiplet, while the enolic proton resonates at $\delta 10.46$ as a 1.2 Hz doublet owing to coupling to H^b in accordance with the so-called W rule [140]. In complex **11b** the enolic proton is lost and the ethoxycarbonyl group now occupies the *anti* position, the ethyl CH_2 protons showing a simple quartet. Free rotation around the C–C bond may equalize the time-averaged environments of the methylene protons. On the other hand the methine proton H^a appears as a doublet coupling to the *syn* H^c proton [129].

Solubilities of complexes **11a** and **11b** in organic solvents are poor, but their suspensions in dichloromethane reacted with tertiary phosphines at room temperature to afford much more soluble complexes in 86–93% yields, $Pd(\eta^3\text{-acac}^{2-})(dpe)$ (**11c**), $Pd(\eta^3\text{-acac}^{2-})(dppe)$ (**11d**), $Pd(\eta^3\text{-etac}^{2-})(dpe)$ (**11e**), $Pd(\eta^3\text{-etac}^{2-})(dppe)$ (**11f**), and $Pd(\eta^3\text{-etac}^{2-})(PPh_3)_2$ (**11g**), where dpe = *cis*-1,2-bis(diphenylphosphino)ethylene and dppe = 1,2-

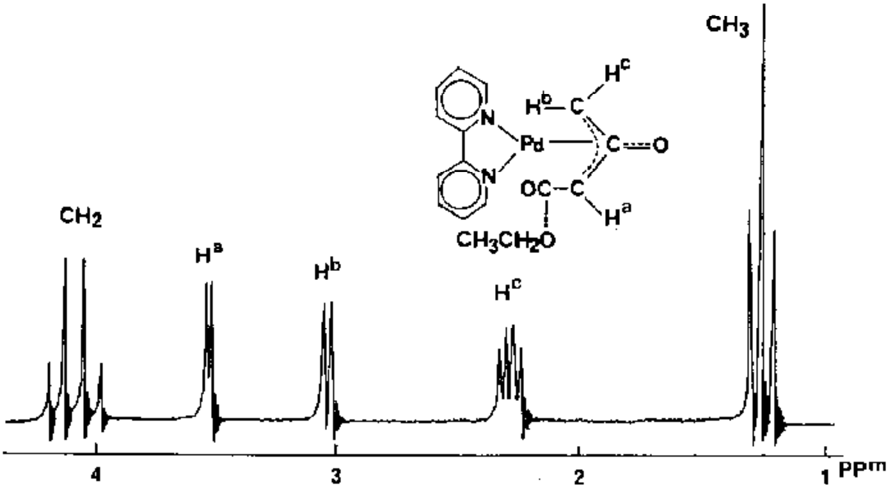


Fig. 10. ^{1}H NMR spectrum of Pd(η^3-etac^{2-})(bpy) in CD_2Cl_2 [129]. Signals from the bipyridine-ring protons are omitted. J(bc) = 4.4 Hz and J(ac) = 2.3 Hz.

bis(diphenylphosphino)ethane. They were characterized mainly by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy and used as starting complexes for preparation of dinuclear complexes containing a β-dik^{2-} ion as a bridging ligand (see section D(vi)) [141].

A Pt(II) complex containing an acac^{2-} ion as a trihapto ligand, Pt(η^3-acac^{2-})$\{P(p\text{-}ClC_6H_4)_3\}_2$, was prepared by the reaction of $Pt(acac)_2$ with tris(p-chlorophenyl)phosphine in chloroform under nitrogen at room temperature in a 49% yield [142]. This complex reacted with pyridinium perchlorate in a mixture of acetone and dichloromethane at 40°C to afford $[Pt(CH_2COCH_2COCH_3)(py)\{P(p\text{-}ClC_6H_4)_3\}_2]ClO_4$ in 64% yield. The terminal-carbon-bonded acac in this complex is exclusively enol, indicating that the $\{(py)(PR_3)_2PtCH_2\}$ moiety serves as a strong electron-withdrawing substituent comparable to the CF_3 group, although $\{(bpy)ClPdCH_2\}$ is electron releasing (section C(vi)).

Recently a series of platinum(II) complexes $\mathrm{P\overline{t(CHRCOC}HR)L_2}$ was prepared by the reactions of $Pt(CO_3)L_2$ with esters of 3-oxopentanedioic acid [143] or 2,4,6-heptanetrione [138], where R = COOMe, L = PPh_3, $AsPh_3$, $PMePh_2$, PMe_2Ph, $\frac{1}{2}Ph_2PCH_2CH_2PPh_2$; R = COOEt, L = PPh_3, $AsPh_3$; R = COOPr^n, L = PPh_3, $AsPh_3$. Similar palladium(II) complexes $\mathrm{P\overline{d(CHRCOC}HR)L_2}$ (R = COOMe, L = PPh_3, $PMePh_2$, PMe_2Ph, PEt_3, $AsPh_3$, $\frac{1}{2}$bpy; R = COOEt, L = PPh_3, $AsPh_3$, $\frac{1}{2}$bpy; R = COOPr^n, L_2 = bpy) were also obtained from the reactions of $[Pd_2(dba)_3]\cdot CHCl_3$ (dba = dibenzylideneacetone) with esters of 3-oxopentanedioic acid in diethyl ether in the presence of donor ligand L and dioxygen [144].

X-ray diffraction studies on $\mathrm{[P\overline{t\{CH(COOMe)COC}H(COOMe)\}(PPh_3)_2]}$

$\cdot$ H_2O [143], $\overline{\mathrm{Pt\{CH(COMe)COC}}\mathrm{H(COMe)\}(PPh_3)}$ [138], and $[\overline{\mathrm{Pd\{CH(COOMe)COC}}\mathrm{H(COOMe)\}L_2] \cdot H_2O}$ ($L = PPh_3$, $AsPh_3$, $\frac{1}{2}$bpy) [144] showed the presence of highly non-planar metallacyclic rings and indicated that a bonding description of these complexes should include a contribution from the η-allylic structure $M(\eta^3\text{-CHRCOCHR})L_2$.

(v) *C,O-Chelation*

$Pt(tfac)_2$ reacted with PPh_3, $P(p\text{-}ClC_6H_4)_3$ and $AsPh_3$ in diethyl ether or chloroform at room temperature to give the $Pt(tfac^{2-}\text{–}C,O)L_2$ complexes in 55, 39 and 87% yields, respectively [145]. The ^1H NMR monitoring revealed that when $Pt(tfac)_2$ was mixed with twice molar PPh_3 in $CDCl_3$, $[Pt(tfac)(PPh_3)_2](tfac)$ was first produced and then converted into $Pt(tfac^{2-}\text{–}C,O)(PPh_3)_2$ [95]. The chelating tfac ligand may have been deprotonated by the tfac anion in the outer sphere.

$Pd(tfac)_2$ reacted readily with an equimolar amount of bpy in benzene at room temperature to yield [Pd(tfac)(bpy)](tfac) [92]. When it was isolated and dissolved in hot dichloromethane, the type **4** complex changed spontaneously to $Pd(tfac^{2-}\text{–}C,O)(bpy)$ [146]. The reaction of $Pd(tfac)_2$ with twice molar PPh_3 in $CDCl_3$ was also confirmed by ^1H NMR spectroscopy to form

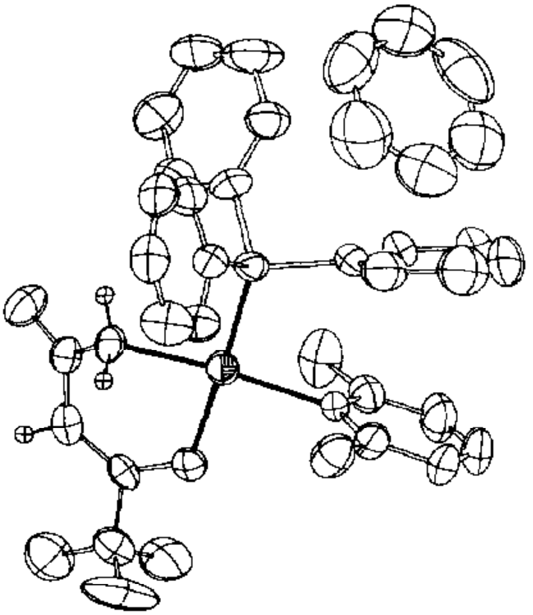
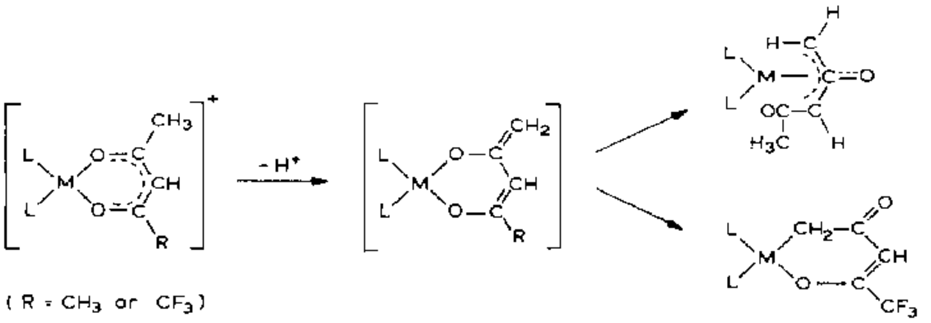


Fig. 11. The molecular structure of $[Pd(tfac^{2-}\text{–}C,O)(PPh_3)(2,6\text{-}Me_2\text{-}py)](C_6H_6)$ [146]. Hydrogen atoms involved only in the $tfac^{2-}$ ligand are drawn. The dihedral angle between the coordination plane and the dimethylpyridine ring is 83.80(15)°.

$[Pd(tfac)(PPh_3)_2](tfac)$ [95]. Contrary to the Pt(II) case, however, the Pd(II) compound is stable and the proton transfer reaction does not occur spontaneously. A powerful and noncoordinating base, 1,8-bis(dimethylamino)-naphthalene (proton sponge) is effective for deprotonation, giving rise to $Pd(tfac^{2-}{-}C,O)(PPh_3)_2$. Employment of pyridine and its derivatives as a base effected substitution of one PPh_3 molecule besides deprotonation of the chelating tfac to result in $Pd(tfac^{2-}{-}C,O)(PPh_3)L$. The molecular structure of $Pd(tfac^{2-}{-}C,O)(PPh_3)(2,6\text{-}Me_2\text{-}py)$ was determined by means of X-ray diffraction (Fig. 11) [146].

Deprotonation of the chelating β-dik ligand in $[M(\beta\text{-dik})L_2]^+$ may produce a dienediolate chelate, which is not stable in the Pt(II) and Pd(II) cases and is transformed into more suitable coordination modes (eqn. (7)). The $tfac^{2-}$ ion prefers C,O-chelation both for Pt(II) and Pd(II), whereas the $acac^{2-}$ ion favors the trihapto coordination over C,O-chelation in either case.



(7)

In the case of $Pt\{\overline{OC(CHCOPh)CHC(Ph)O}\}(PPh_3)_2$ (section D(ii)), the presence of phenyl groups in the dianion of triketone may prevent transformations of the above type, thus stabilizing the dienediolate structure [138].

(vi) η^3,O,O′-Bridging

Each of the trihapto dianionic ligands in **11a–11g** still has uncoordinated oxygen atoms, suggesting the possibility of interaction with another metal atom. In fact, complexes **11c–11g** reacted with $[Pd(PP)(H_2O)_2](ClO_4)_2$ (PP = dpe or dppe) in methanol at 0°C to give the $[(PP)Pd(\eta^3\text{-}\beta\text{-}dik^{2-}{-}O,O')Pd(PP)](ClO_4)_2$ complexes in 55–83% yields. Unfortunately single crystals of these compounds suitable for X-ray analysis have not been obtained, but their structures were inferred from the ^1H, ^{13}C, and ^{31}P NMR spectra [141]. Figure 12 exemplifies the ^{13}C NMR signals from the $etac^{2-}$ ligand in $[(dpe)Pd(\eta^3\text{-}etac^{2-}{-}O,O')Pd(dpe)](ClO_4)_2$, which accord with the proposed dinuclear structure. Some other mixed-metal dinuclear complexes

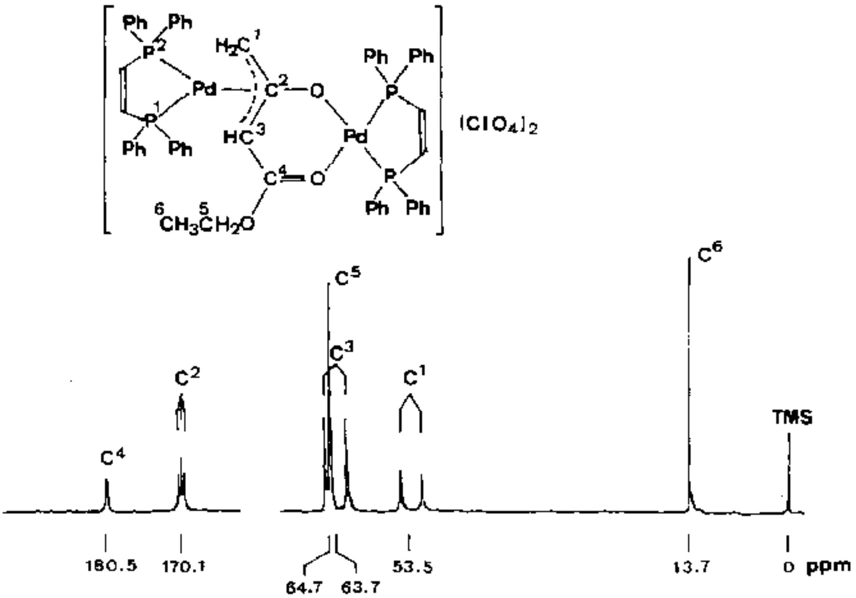


Fig. 12. $^{13}C\{^1H\}$ NMR signals at 15.04 MHz from the etac^{2-} ligand in [(dpe)Pd(η^3-etac^{2-}-O,O')Pd(dpe)](ClO$_4$)$_2$ in acetone-d_6 [141]. $J(P^1-C^1) = 43$ Hz, $J(P^1-C^2) = J(P^2-C^2) = 6$ Hz, and $J(P^2-C^3) = 33$ Hz.

containing Pd(II) and Pt(II), Ni(II) or Mg(II) have also been prepared but their characterization is not satisfactory [141].

E. η^3,C,O-BRIDGING OF THE ACETYLACETONATE TRIANION

In the course of research for the dianion complexes, Okeya et al. [147] have recently obtained a dinuclear Pt(II) complex containing a trianion of acetylacetone as the η^3,C,O-bridging ligand. In hot methanol Pt(acac)$_2$ reacted readily with a twice molar amount of PPh$_3$ to afford [Pt(acac)(PPh$_3$)$_2$](acac). When the mixture was kept at 60°C for more than

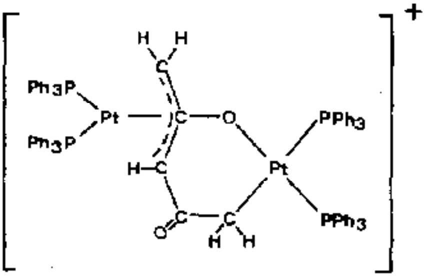


Fig. 13. The dinuclear structure proposed for [Pt$_2$(C$_5$H$_5$O$_2$)(PPh$_3$)$_4$]$^+$ [147].

four hours, a novel dinuclear complex $[Pt_2(C_5H_5O_2)(PPh_3)_4](acac)$ (**13a**) was produced together with a small amount of $Pt(\eta^3\text{-}acac^{2-})(PPh_3)_2$. The yield of **13a** in solution was estimated by ^{31}P NMR spectroscopy to be 80–90%. Light brown crystallites of **13a** were obtained in 45% yield (on the basis of Pt) on twice recrystallization from dichloromethane/n-pentane. Addition of KPF_6 to the reaction mixture gave white crystals of $[Pt_2(C_5H_5O_2)(PPh_3)_4]PF_6$ (**13b**) in 56% yield.

$$2\ Pt(acac)_2 \xrightarrow{+4\ PPh_3} 2\left[Pt(acac)(PPh_3)_2\right](acac) \rightarrow \underset{\textbf{13a}}{\left[Pt_2(acac^{3-})(PPh_3)_4\right](acac)}$$

$$\xrightarrow{+KPF_6} \underset{\textbf{13b}}{\left[Pt_2(acac^{3-})(PPh_3)_4\right]PF_6}$$

The ^1H, ^{13}C, ^{31}P and ^{195}Pt NMR spectroscopic data for **13a** and **13b** are consistent with the proposed structure of the complex cation in which the acetylacetonate trianion coordinates with a Pt(II) atom in a trihapto fashion and C,O-chelates another Pt(II) atom (Fig. 13) [147].

F. CONCLUDING REMARKS

Although β-dicarbonyl compounds are very classic as ligands, a number of new coordination modes of their mono- and dianions have been explored only in recent years. Their preference for η^1 and η^3 carbon bonding to the usual O,O′-chelation has been demonstrated mostly in the Pd(II) and Pt(II) complexes. It is hoped, however, that many complexes of other metals containing β-dik ligands in non-classical coordination states will be prepared in the future, and that the role of β-dik ligands in various metal complex reactions will be elucidated. The $acac^{2-}$ and $etac^{2-}$ ions stabilized in the coordination sphere of Pd(II) may be useful for organic syntheses, since the acetoacetate dianion is one of the fundamental building blocks in the biogenesis of natural products [148].

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