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1,4-Diazabutadiene Olefin Complexes of Zerovalent Palladium: Preparation and Characterization

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A number of mixed olefin diazabutadiene (RN:CR'CR':NR; DAB) complexes of zero-valent palladium [(olefin)Pd(DAB)] have been prepared by the simultaneous reactions of an activated olefin and a DAB with an appropriate source of Pd(0). The complexes have been characterized by ^1H–^{13}C NMR, I.R. and Raman spectroscopy. The physical and chemical properties of the complexes are dependent upon the olefin and DAB ligands employed. Complexes where olefin = dimethylfumarate(dmf) or diethylfumarate (def) and DAB = tBuN:CHCH:NtBu (DAB^{H}_{tBu}) readily undergo ligand displacement reactions with PPh_3 and tBuNC (leading to displacement of the DAB), oxidative addition with methylallyl chloride (leading to displacement of the olefin) yielding a dinuclear Pd(II) complex, ([(methylallyl)(chloride)Pd]$_2$tBuN:CHCH:NtBu) and react with excess olefin yielding a dinuclear Pd(0) complex ([(olefin)$_2$Pd$_2$]tBuN:CHCH:NtBu).

Introduction

Many diazabutadiene (DAB) complexes of zero valent transition metals, often with carbon monoxide as coligand, have been prepared by tom Dieck and coworkers [1–11] and Vrieze, Staal *et al.* [12–16] and the spectroscopic properties of a number of these complexes have been extensively studied [2, 5, 12, 13, 18–22] (Fig. 1). Due to the versatile stabilizing influence of the carbonyl ligands the mixed DAB–CO complexes have been shown to exhibit particularly exciting chemical activity, both at the metal centre(s) and at the DAB ligand. Reactions involving metal–metal bond formation [14–15], 'σ, π' bridging coordination of the DAB ligand (*i.e.* the DAB becomes a 6-electron donor) [16, 17], activation of the C=N bond resulting in C–C bond formation between two DAB ligands [15, 16] and insertion of unsaturated molecules between the DAB and the metal centre [23], have been observed.

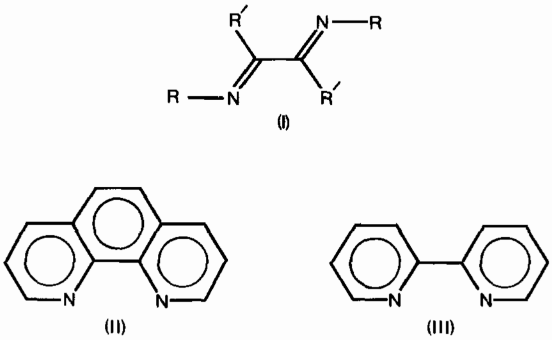

Fig. 1. DAB and related ligands: (1) DAB, (11) 1,10-phenanthroline, (111)2,2'-bipyridine.

Studies on metal DAB complexes of the nickel group metals, in particular studies on the zerovalent metals, have been almost entirely confined to nickel itself. The earliest reports of Ni(0)DAB complexes in the literature are those of Balch and Holm [24], who prepared the complex bis(biacetylbisanil)nickel(0), and Bock and tom Dieck [10] who prepared bis(carbonyl)diazabutadiene nickel(0) complexes. Since then Walther has reported the preparation of several Ni(0)DAB complexes from $Ni(COD)_2$ (where COD = 1,5-cyclooctadiene) $Ni(CO)_4$ and $Ni(PPh_3)_2(C_2H_4)$; both mono and bis DAB complexes were isolated [25, 26]. Several groups have also prepared various mixed Ni(0) complexes containing the DAB-related 2,2-bipyridine (bipy) as a ligand [27–30]. A crystal structure analysis of the complex dicarbonyldiacetylbis(dimethoxyhydrazone)nickel(0) has been published by Hausen and Krogmann [31]. Recently tom Dieck and coworkers have prepared a range of bis(DAB)Ni(0) complexes by direct reduction of Ni(11)DAB complexes with sodium metal in the presence of DAB ligand [32]. The bis DAB complexes were found to exhibit interesting chemical behaviour including catalytic activity. These authors also reported the preparation of an unusual dimeric Ni(I)-DAB complex containing bridging bromine atoms and a metal–metal bond.

The preparations of several M(II)DAB complexes (where M(II) = Pd(II) and Pt(II)), with the DAB in

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various coordination modes, have recently been published [33–37]. The only DAB complexes of Pt(0) reported in the literature to date are mixed DAB–COD complexes prepared by the reaction of DAB ligand with $Pt(COD)_2$ [38]. No complexes of Pd(0) with simple DAB ligands have been reported. Ishii and coworkers have prepared a number of Pd(0) complexes of the more rigid, conjugated α-diimines 2,2-bipyridine(bipy) and 1,10-phenanthroline(phen) [39–41]. The properties of such ligands are known to be considerably different to that of the DAB ligands, these differences are further born out by the present study. Ishii *et al.* have prepared the complexes $(DBA)Pd(L_2)$ (where DBA = dibenzylideneacetone, L_2 = bipy or phen) [39, 41] and $(TBAA)_2Pd_3(bipy)_3$ (where TBAA = tribenzylideneacetylacetone) [40] by the direct reaction of the appropriate ligand with $Pd_2(DBA)_3 \cdot CHCl_3$ or $Pd_3(TBAA)_3 \cdot CHCl_3$. Further reaction of these bipy and phen complexes with various activated olefins yielded mixed olefin–L_2 complexes.

As part of a continuing programme of research on metal–diazabutadiene complexes being undertaken in this laboratory a range of Pd(0) DBA complexes have been prepared and their chemistry studied. We report herein a series of complexes (olefin)Pd(RN:CR′CR′:NR), where olefin = tetracyanoethylene (TCNE), R = tBu R′ = H; olefin = maleic anhydride (MA), R = tBu R′ = H, R = iPr R′ = H, R = cHex R′ = H; olefin = dimethylfumarate (dmf), R = tBu R′ = H, R = cPr R′ = CH_3, R = $[(CH_3)_2CH]_2CH$-R′ = H, R = p-CH_3O-(C_6H_4)-R′ = H; olefin = diethylfumarate (def), R = tBu, R′ = H, R = p-$CH_3O(C_6H_4)$-R′ = H.

Structural and bonding features of the complexes have been elucidated (^1H–^{13}C NMR, IR, Raman) and various reactions (including ligand exchange and oxidative addition) of representative complexes are described.

Results and Discussion

Preparation and Properties of (olefin)Pd(DAB) Complexes

As $Pd(CO)_4$ is unknown and $Pd(COD)_2$ is thermally unstable the sources of Pd(0) employed in this work were the complexes of Ishii and coworkers, $Pd(DBA)_2$ [39, 42], $Pd_2(DBA)_3 \cdot CHCl_3$ [39] and $Pd_3(TBAA)_3 \cdot CHCl_3$ [40]. The complex $Pd_3(TTAA)_3$ (TTAA = tritoluylideneacetylacetone) was also prepared and employed as starting material. The TTAA ligand and the $Pd_3(TTAA)_3$ complex were prepared by a method similar to that employed by Ishii *et al.* for the preparation of TBAA and $Pd_3(TBAA)_3 \cdot CHCl_3$ [40]. The TTAA ligand is only sparingly soluble in methanol, consequently in the preparation of the zerovalent Pd complex a large volume of methanol is required to prevent contamination of the final complex by free TTAA. The low solubility of the TTAA ligand was used to advantage in the isolation of the more soluble and labile complexes prepared in this work.

Unlike the reactions of bipy or phen, the treatment of Pd DBA, TBAA or TTAA complexes with excess DAB ligand did not generally yield a complex of the type (Lig)Pd(DAB) (Lig = DBA, TBAA, TTAA). Although the DAB ligands are thought to be stronger π-acceptors than bipy or phen [7–9, 43] they are also strong σ-donors and the overall effect of complexation to a metal is to concentrate electron density at the metal centre, probably to a greater extent than bipy or phen. Thus only when the basicity of the DAB ligand was reduced, *i.e.* by the presence of strong electron withdrawing substituents, was it possible to isolate a complex containing DBA and DAB.

To obtain stable DAB complexes of zerovalent Pd it was necessary to react the DAB ligand with the appropriate starting complex in the presence of a strong acceptor ligand *e.g.* an activated olefin. The high basicity of the DAB ligand, in particular the aliphatic DAB's limited the type of acceptor coligands that could be used. However, the variety of DAB ligands that can be prepared and the variety of activated olefins available meant that the physical and chemical properties of the resulting complex can be controlled by employing olefins of varying acceptor ability or by varying the DAB used. The balance of electron density movement (*i.e.* push–pull effect) has previously been recognized as being important for the preparation of zerovalent Ni group metal complexes [44]. However, this effect has generally only been considered for homoligand complexes and the so-called synergic (σ-donor, π-acceptor) mechanism is usually discussed. It is evident that a similar mechanism for the control of electron density on the metal centre can occur for complexes containing a mixture of ligands, *i.e.* the types of complexes studied in this work. In effect electron density may be considered as being transferred from the donor ligand(s) (in this case DAB) across the metal centre to the acceptor ligand(s) (in this case activated olefin).

Consideration of this donor–acceptor mechanism enabled Ishii *et al.* to prepare a series of mixed olefin Pd(0) complexes of varying stability [45]. It was found that a judicious choice of electron donating and electron withdrawing olefins was necessary to obtain stable Pd(0) complexes.

For the preparation of the complexes where olefin = dmf, and def, DAB = (tBuN:CHCH:NtBu), $Pd_3(TTAA)_3$ was preferred as the source of Pd(0). The dmf and def complexes are very soluble in many organic solvents and are extremely labile. During work up of these complexes the back reaction, yielding the starting Pd(0) complex easily occurs, this

TABLE I. Analytical and I.R. Data for (olefin)Pd(RN:CR′CR′:NR)[a].

Compound	C (%)	H (%)	O (%)	N (%)	IR (cm^{-1})	Molecular Weight
1 (TCNE)Pd(tBuN:CHCH:NtBu)	47.55 (47.69)	5.09 (5.01)	–	20.98 (20.87)	ν(C≡N); 2165(s)	
2 (MAH)Pd(tBuN:CHCH:NtBu)	45.24 (45.09)	6.00 (5.95)	13.17 (12.88)	7.59 (7.52)	ν(C=O); 1795(vs), 1760(s), 1725(vs)	370 (372.4)
3 (MAH)Pd(iPrN:CHCH:NiPr)	42.01 (41.80)	5.24 (5.27)	14.06 (13.93)	8.15 (8.13)	ν(C=O); 1798(vs), 1763(m), 1723(vs)	
4 (MAH)Pd(cHexN:CHCH:NcHex)	50.78 (50.87)	6.07 (6.17)	11.59 (11.30)	6.47 (6.60)	ν(C=O); 1798(vs), 1759(m), 1725(vs)	
5 (dmf)Pd(cPrN:CCH_3CCH_3:NcPr)	46.11 (46.31)	5.74 (5.83)	15.31 (15.43)	6.68 (6.76)		
6 (dmf)Pd(*p*-$CH_3OC_6H_4N$:CHCH:N*p*-$CH_3OC_6H_4$)	50.49 (50.91)	4.67 (4.66)	18.62 (18.51)	5.41 (5.40)	ν(C=O); 1690(vs), 1675(vs)	
7 (def)Pd(*p*-$CH_3OC_6H_4N$:CHCH:N*p*-$CH_3OC_6H_4$)	52.38 (52.69)	5.12 (5.16)	17.32 (17.56)	5.06 (5.12)	ν(C=O); 1690(s), 1670(s)	486 (546.7)
8 (dmf)Pd(tBuN:CHCH:NtBu)	45.69 (45.89)	6.77 (6.74)	15.52 (15.28)	6.61 (6.69)	ν(C=O); 1685 (broad, vs)	397 (418.8)
9 (def)Pd(tBuN:CHCH:NtBu)	48.32 (48.36)	7.17 (7.22)	14.23 (14.33)	6.18 (6.27)	ν(C=O); 1675 (broad, vs)	
10 (dmf)Pd($[CH_3)_2CH]_2CHN$:CHCH:$NCH[CH(CH_3)_2]_2$)	52.84 (52.52)	8.12 (8.02)	12.64 (12.73)	5.38 (5.57)	ν(C=O); 1690(s), 1677(s)	
11 $(DBA)_2Pd_2$(*p*-ClC_6H_4N:CHCH:N-*p*-ClC_6H_4)	62.33 (59.49)	4.23 (3.87)	2.29 (2.76)		ν(C=O); 1645(s)	

[a] Calculated analytical data are given in parenthesis. I.R. data was obtained by KBr disc.

TABLE II. ^{1}H NMR Chemical Shifts for (olefin)Pd(DAB) in $CDCl_3$ Solution. δ(ppm) Relative to TMS.

Compound	δ(ppm)[a]
1 (TCNE)Pd(tBuN:CHCH:NtBu)	[b]$\delta(CH_3)_s^{tBu} = 1.52$; $\delta(CH)_s^{imine} = 8.45$
2 (MAH)Pd(tBuN:CHCH:NtBu)	$\delta(CH_3)_s^{tBu} = 1.42$; $\delta(CH)_s^{olefinic} = 3.81$; $\delta(CH)_s^{imine} = 8.07$
3 (MAH)Pd(iPrN:CHCH:NiPr)	$\delta(CH_3)_m^{i\text{-}propyl} = 1.35$; $\delta(CH)_{sept.}^{i\text{-}propyl} = 3.85$; $\delta(CH)_s^{olefinic} = 3.90$; $\delta(CH)_s^{imine} = 8.10$
4 (MAH)Pd(cHexN:CHCH:NcHex)	$\delta(CH_2)_{b.m.}^{cHex} = 1.70$; $\delta(CH)_{b.m.}^{cHex} = 3.42$; $\delta(CH)_s^{olefinic} = 3.86$; $\delta(CH)_s^{imine} = 8.07$
5 (dmf)Pd(cPrN:CCH_3CCH_3:NcPr)	$\delta(CH_2)_m^{cPr} = 1.10$; $\delta(CH_2)_m^{cPr}$; 1.50; $\delta(CCH_3)_s^{DAB} = 2.22$; $\delta(CH)_{sex.}^{cPr} = 3.10$; $\delta(CH)_s^{olefinic} = 3.55$; $\delta(CH_3)_s^{olefin} = 3.58$
7 (def)Pd(p-$CH_3OC_6H_4N$:CHCH:N-p-$CH_3OC_6H_4$)	$\delta(CH_3)_t^{olefin} = 1.20$; $\delta(OCH_3)_s^{DAB} = 3.75$; $\delta(CH)_s^{olefinic} = 3.78$; $\delta(CH_2)_m^{olefin} = 4.00$; $\delta(CH)_{AB}^{aromatic} = 7.10$; $\delta(CH)_s^{imine} = 8.35$
8 (dmf)Pd(tBuN:CHCH:NtBu)	$\delta(CH_3)_s^{tBu} = 1.40$; $\delta(CH_3)_s^{olefin} = 3.59$; $\delta(CH)_s^{olefinic} = 3.76$; $\delta(CH)_s^{imine} = 8.05$
9 (def)Pd(tBuN:CHCH:NtBu)	$\delta(CH_3)_m^{olefin} = 1.20$; $\delta(CH_3)_s^{tBu} = 1.40$; $\delta(CH)_s^{olefinic} = 3.75$; $\delta(CH_2)_m^{olefin} = 4.05$; $\delta(CH)_s^{imine} = 8.02$
10 (dmf)Pd($[(CH_3)_2CH]_2CHN$:CHCH:$NCH[CH(CH_3)_2]_2$)	$\delta(CH_3)_m^{DAB} = 1.00$; $\delta(CH)_m^{DAB} = 2.40$; $\delta(CH_3)_s^{olefin} = 3.48$; $\delta(CH)_s^{olefinic} = 3.52$; $\delta(CH)_s^{imine} = 7.73$

[a] s = singlet, m = multiplet, sept = septet, b.m. = broad unresolved multiplet, t = triplet, AB = AB pattern, sex = sextet. [b] d_6-acetone was used as solvent.

was particularly so when $Pd(DBA)_2$ or $Pd_2(DBA)_3 \cdot CHCl_3$ was employed as the source of Pd(0). Further, large excesses of olefin ligand could not be used, as under these conditions an unstable white complex formed. (This same product was prepared by the reaction of isolated (olefin)Pd(DAB) with excess olefin and was identified as the dinuclear Pd(0) complex $[(olefin)_2Pd]_2DAB$, containing a bridging DAB). When $Pd_3(TTAA)_3$ was employed as the starting material and a minimum of solvent was used for the reaction much of the displaced TTAA precipitated and could be filtered off before the back reaction could occur. (However, reaction times were much longer employing this complex instead of the Pd(DBA) complexes as starting material).

All the (olefin)Pd(DAB) complexes prepared were found to be air stable in the solid state, however in solution palladium metal was slowly deposited.

Structure of and Bonding in (olefin)Pd(DAB) Complexes

It is evident from the analytical and spectroscopic data that the (olefin)Pd(DAB) complexes prepared in this work are monomeric with C_{2v} symmetry in solution and with palladium having a sixteen electron valence shell. Whether the complexes are best described as three coordinate or four coordinate is arguable and depends on the mode of coordination of the olefin, structures I and II representing the extreme cases, *i.e.* I being pure donor bonding and II representing acceptor bonding [46]. Methods for assessing the importance of structures I and II in various metal complexes containing bound olefins have been discussed in detail elsewhere [44]. However, the reliability of the various techniques for such assessments is still questionable and in most cases the 'true' structure lies somewhere between I and II. There can be little doubt that in the complexes studied in the present work structure II plays an important role. It is evident from ^1H and ^{13}C NMR data (Tables II and III) that the electronic structure of the olefin is greatly modified on complexation. In the ^1H NMR of the complexes the resonance due to the olefinic protons is shifted 2.5–3 ppm upfield compared with the free olefin and the olefinic carbon atom resonance appears in the aliphatic region of the ^{13}C spectra. In contrast the changes in the NMR spectra of the DAB ligands on complexation are

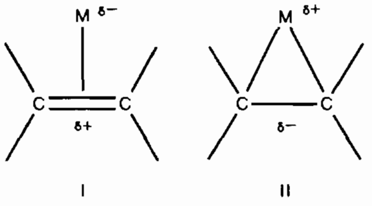

Fig. 2. Extreme electronic structures.

TABLE III. ^{13}C NMR Chemical Shifts for (olefin)Pd(DAB) in $CDCl_3$ Solutions. δ (ppm) relative to TMS.[a]

Compound	
2 (MAH)Pd(tBuN:CHCH:NtBu)	$\delta(CH_3)^{tBu} = 29.47$; $\delta(CH)^{olefinic} = 40.90$; $\delta(C)^{tBu} = 62.57$; $\delta(CH)^{imine} = 156.20$; $\delta(CO)^{olefin} = 172.60$
5 (dmf)Pd(cPrN:CCH$_3$CCH$_3$:NcPr)	$\delta(\text{-CH-})_d^{cPr} = 10.74$; $\delta(\text{-CH}_3)^{DAB} = 17.86$; $\delta(\text{N-CH-})^{cPr} = 36.62$; $\delta(CH)^{olefinic} = 41.22$; $\delta(\text{-OCH}_3)^{olefin} = 50.99$; $\delta(N{=}C)^{imine} = 168.05$; $\delta(C(0)O)^{olefin} = 175.28$
8 (dmf)Pd(tBuN:CHCH:NtBu)	$\delta(CH_3)^{tBu} = 28.63$; $\delta(CH)^{olefinic} = 40.77$; $\delta(OCH_3)^{olefin} = 49.91$; $\delta(C)^{tBu} = 60.96$; $\delta(CH)^{imine} = 155.30$; $\delta(C(0)O)^{olefin} = 174.36$
9 (def)Pd(tBuN:CHCH:NtBu)	$\delta(CH_3)^{olefin} = 14.35$; $\delta(CH_3)^{tBu} = 29.31$; $\delta(CH)^{olefinic} = 41.88$; $\delta(OCH_2)^{olefin} = 59.02$; $\delta(C)^{tBu} = 61.52$; $\delta(CH)^{imine} = 155.52$; $\delta(C(0)O)^{olefin} = 174.67$
10 (dmf)Pd([(CH$_3$)$_2$CH]$_2$CHN:CHCH:NCH[CH(CH$_3$)$_2$]$_2$)	$\delta(CH_3)_q^{DAB} = 19.30$; $\delta(CHMe_2)_d^{DAB} = 30.08$; $\delta(CH)^{olefinic} = 43.26$; $\delta(\text{-OCH}_3)^{olefin} = 50.41$; $\delta(\text{N-CH})^{DAB} = 84.22$; $\delta(CH)^{imine} = 157.52$; $\delta(C(0)O)^{olefin} = 174.68$.

[a] m = multiplet, q = quartet, d = doublet.

relatively small. Shifts in the position of lines due to the imine protons varied between 0.5 and 0 ppm downfield. The proposed structure of the (olefin)Pd(DAB) complexes is shown in Fig. 3. The trigonal-planar structure proposed is that commonly encountered in 'three-coordinate' d^{10} complexes containing an unsaturated molecule as a ligand [47].

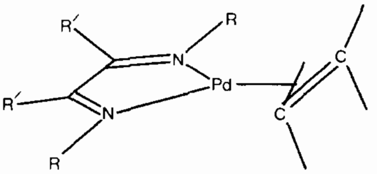

Fig. 3. The proposed structure of the (olefin)Pd(DAB) complexes. Substituents on the olefin have been omitted for simplicity.

Further evidence for the changes in the ligands on complexation is obtained from the Raman spectra of selected complexes and ligands (Table IV). For the complexes studied there was no band above 1350 cm^{-1} which could be assigned to the olefin ν(C=C). Rather weak bands were observed in the region of 1250 cm^{-1} which were tentatively assigned to (C=C) stretching vibrations, realizing the probability of coupling with other vibrations within the olefin ligand [46]. The strong band which occurred at approximately 1586 ± 10 cm^{-1} in the Pd DAB complexes was assigned to the symmetrical (C=N) stretch, this band is absent or weak in the corresponding I.R. spectra. The band is shifted some 60 cm^{-1} to lower frequency compared with the free DAB ligand, which reflects the relatively small perturbation to the C=N bonds on complexation, in agreement with NMR data and chemical behaviour.

A small but distinctive trend in the position of the ν_s(C=N) band for the complexes considered is evident and may reflect the relative degree of involvement of the C=N bonds on complex formation and in turn appears to mirror the difference in π-acidity of the olefin ligands. For the complex containing the very strong acceptor olefin TCNE, ν_s(C=N) occurs at 1598 cm^{-1}, whilst for the complex with MAH, a weaker acceptor, ν_s(C=N) occurs at 1585 cm^{-1} and finally for the complex with dmf, a still weaker acceptor, ν_s(C=N) appears at 1578 cm^{-1}.

A comparison of (C≡N) stretching frequencies in free TCNE [48], (TCNE)Pd(DAB) and $TCNE^-$ [48, 49] provides information regarding charge density on the olefin in the Pd complex. In free TCNE strong bands assigned to ν(C≡N) [48] occur at 2250 (A_g) and 2237 cm^{-1} (B_{1g}), whilst for the $TCNE^-$ anion bands appear around 2200 cm^{-1} (symmetrical stretching vibrations) [48, 49]. Thus it is evident that there is a shift of ν_s(C≡N) to lower wavenumbers when there is build up of charge on the olefin. For the (TCNE)Pd(tBuN:CHCH:NtBu) complex strong bands occur at 2232, 2224 and 2214 cm^{-1} *i.e.* lower than free TCNE and higher than $TCNE^-$, thus indicating significant charge build up on the TCNE in the complex.

Strong bands around 450 cm^{-1} in the complexes have been tentatively assigned to ν_s(Pd–C). No bands which could be assigned to ν_s(Pd–N) were observed.

The DAB ligands $[(CH_3)_2CH]_2CH$–N:CHCH:N–$CH[CH(CH_3)_2]_2$ and cPrN:CCH_3CCH_3:NcPr each contain three different prochiral centres (Fig. 4). On complexation full chirality is induced at each centre, as evidenced by the ^1H and ^{13}C NMR. In the ^{13}C NMR spectrum of complexed ligand (a) (Fig. 4a), four lines are observed for the methyl carbon atoms

TABLE IV. Main Bands Observed in the Raman Spectra of Selected Compounds[a].

Compound	Main Bands and Proposed Assignments	
tBuN:CHCH:NtBu	1646(s)	ν(C=N)
$(MAH)Pd(PPh_3)_2$	1790(m), 1775(m), 1718(m)	ν(C=O)
	1578(m), 1564(w)	ν(C=$C^{aromatic}$)
	1345(w)	ν(C=C^{olefin})
(MAH)Pd(tBuN:CHCH:NtBu)	1793(s), 1764(w), 1722(s)	ν(C=O)
	1585(s)	ν_s(C=N)
	1245(w), 1230(w)	ν(C=C)
	442(s)	ν_s(Pd–C)
(TCNE)Pd(tBuN:CHCH:NtBu)	2232(s), 2224(s), 2214(m)	ν(C≡N)
	1598(s)	ν_s(C=N)
	1334(w), 1239(m), 1210(w)	ν(C=C)
(dmf)Pd(tBuN:CHCH:NtBu)	1578(s)	ν_s(C=N)
	454(s)	ν_s(Pd–C)

[a] Spectra were obtained on solid samples at approximately –160 °C.

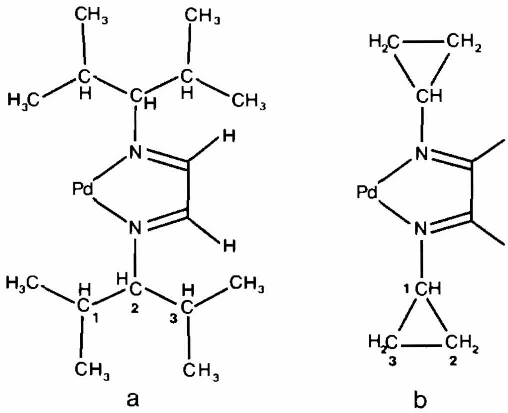

Fig. 4. DAB ligands containing prochiral centres.

and two lines are observed for the isopropyl carbon atoms 1 and 3 (Table III). In the proton NMR of complexed ligand (a) the three C-H groupings 1, 2 and 3 (Fig. 4a) give rise to a complex arrangement of overlapping multiplets in the region 1.7–2.85 ppm and the methyl protons give rise to a second complex set of lines in the region 0.78–1.35 ppm. Similarly the ^{13}C NMR of complexed ligand (b) contains three lines, for the cyclopropyl ring carbons 1, 2 and 3 (Fig. 4b); a doublet centred at 10.74 ppm for carbons 2 and 3 and a line at 36.62 ppm for carbon 1 (Table III). The proton spectrum of this ligand contains two sets of complex multiplets, 2.80–3.28 ppm (cyclopropyl proton, position 1) and 0.70–1.75 ppm (cyclopropyl protons, positions 2 and 3).

Reactions of (olefin)Pd(DAB) Complexes

Reactions of various representative complexes have been studied. These include oxidative addition, ligand exchange and reaction with excess ligand.

The (olefin)Pd(DAB) complexes were found to readily undergo ligand exchange with triphenylphosphine. Reaction of the complexes (olefin)Pd(tBuN:CHCH:NtBu) (where olefin = TCNE, MAH and dmf) with two equivalents of triphenylphosphine in acetone at room temperature gave the compounds (olefin)Pd(PPh_3)$_2$ in high yield. (Olefin)Pd(PPh_3)$_2$ complexes of this type have been previously prepared by other methods [50, 51]. The related Ni(0) and Pt(0) complexes have also been prepared [44].

On stirring the complexes (dmf)Pd(DAB) and (def)Pd(DAB), where DAB = tBuN:CHCH:NtBu, with an excess of olefin ligand the colour of the original complex fades and a white solid is obtained. This solid is insoluble in ether, ethanol, hexane, sparingly soluble in acetone and soluble in chlorinated solvents. Rapid decomposition occurs in solution at room temperature in the absence of free olefin. Low temperature ^{1}H NMR indicates the presence of complexed DAB and olefin in the ratio 1:4. On the basis of ^{1}H NMR and microanalysis data this complex has been postulated as a dinuclear Pd(0) complex containing a bridging DAB with a probable *trans* conformation (Fig. 5). The *trans* conformation has been shown to be the configuration preferred by a bridging DAB [36].

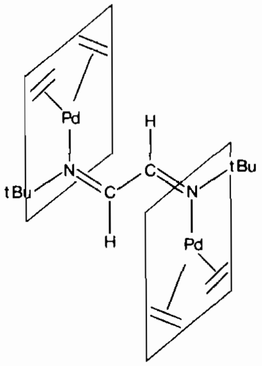

Fig. 5. Proposed structure of the complex ([(dmf)$_2$Pd]$_2$-tBuN:CHCH:NtBu). Substituents on the olefin have been omitted for simplicity.

When ether suspensions of (dmf) or (def) Pd-(tBuN:CHCH:NtBu) are treated with an excess of tBuNC the intense orange yellow colour of the (olefin)Pd(DAB) complex rapidly fades and the complex (olefin)Pd(tBuNC)$_2$ can be isolated in high yield. Related mixed olefin–isocyanide complexes of Pd(0) have been prepared by other methods [52, 53]. The Pt(0) analogues of these mixed olefin-isocyanide complexes have recently been reported by Stone *et al.* [54].

Oxidative addition reactions of methylallylchloride with (dmf) or (def)Pd(tBuN:CHCH:NtBu) led to displacement of the olefin and formation of a (DAB)Pd(II) complex. When methylallylchloride is added to a stirred ether suspension of (olefin)-Pd(DAB^{H}_{tBu}) at room temperature the intense colour of the original complex fades to give a pale yellow solution from which white crystals of the dinuclear DAB bridged complex [(methylallyl)(chloride)Pd]$_2$-DAB^{H}_{tBu} (Fig. 5) were isolated in high yield.

The complex was identified by ^{1}H NMR, I.R. and microanalysis. ^{1}H NMR indicated the presence of complexed tBuN:CHCH:NtBu and methylallyl in the ratio 1:2 and I.R. confirmed the presence of complexed chloride. Microanalysis was in agreement with the proposed formulation. As previously mentioned for the dinuclear Pd(0) complex, Fig. 5, the bridging DAB in [(methylallyl)(chloride)Pd]$_2$-DAB^{H}_{tBu} probably has a *trans* configuration (Fig. 6).

Experimental

All manipulations were carried out under dry oxygen-free nitrogen and all solvents were carefully dried and purified before use. The diazabutadienes were prepared by published methods [2, 55]. The complexes Pd(DBA)$_2$ [39, 42], $Pd_2(DBA)_3 \cdot CHCl_3$ [39]

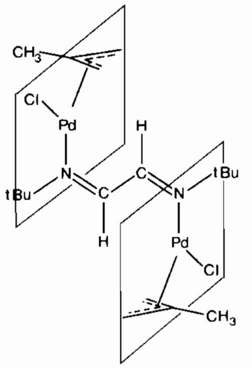

Fig. 6. Proposed structure of the complex ([(methylallyl)(chloride)Pd]$_2$tBuN:CHCH:NtBu).

and $Pd_3(TBAA)_3CHCl_3$ [40] were prepared by published methods. All olefins employed in the preparations are commercially available and were used without further purification.

Microanalyses were carried out by the section Elemental Analyses of the Institute for Organic Chemistry, TNO, Utrecht, The Netherlands. Molecular weights were determined by cryoscopy in chloroform. ^1H NMR spectra were recorded on Varian A 60 and T 60 D spectrometers. ^{13}C NMR spectra were recorded on a Varian CFT 20 spectrometer. Infrared spectra were recorded on Beckman IR 4259 and Perkin Elmer 283 infrared spectrometers. Raman spectra were obtained on a HG 2S Ramanor using a Spectra Physics 171 Ar^+ ion laser and a CR model 490 dye laser with Rhodamine 6G in ethyleneglycol as dye.

Preparation of $Pd_3(TTAA)_3$

This complex was prepared by a variation of the method employed by Ishii *et al.* for the preparation of $Pd_3(TBAA)_3{\cdot}CHCl_3$ [40]. Tritoluylideneacetylacetone was prepared by the alkaline condensation of 0.3 mol *p*-toluylaldehyde and 0.1 mol acetylacetone [40]. (It is essential to use the correct molar ratios of *p*-toluylaldehyde and acetylacetone otherwise an oily product results). The resultant yellow solid was recrystallized from dichloromethane. Yield 60%. $Pd_3(TTAA)_3$ was prepared from 11.5 g (28.3 mmol) TTAA and 2.5 g (14 mmol) $PdCl_2$ in 1500 ml of methanol in the presence of 4.1 g (30 mmol) sodium acetate. The resultant purple crystalline solid was recrystallized from chloroform–ether and obtained in approximately 70% yield. Microanalysis: Found (calc) %C = 66.77 (67.44), %H = 5.60 (5.11), %O = 6.28 (6.24).

Preparation of the Complexes (olefin)Pd(RN:CR′CR′:NR)

The complexes where olefin = TCNE, R = tBu R′ = H; olefin = MAH, R = tBu, R′ = H, R = iPr, R′ = H, R = cHex R′ = H; olefin = dmf, R = cPr R′ = CH_3, were prepared in the following manner.

An acetone (30 ml) suspension of 1.0 mmol Pd(0) (as $Pd(DBA)_2$ or $Pd_2(DBA)_3{\cdot}CHCl_3$) was stirred with 1.1 mmol of the appropriate olefin and 1.1 mmol of the appropriate DAB, at room temperature. Stirring was continued for approximately 3 hours except in the case of (dmf)Pd(cPrN:CCH_3CCH_3:NcPr) where stirring was continued for 24 hours. A dirty yellow to red homogeneous solution was obtained, except for (TCNE)Pd(tBuN:CHCH:NtBu) where a yellow precipitate was also present. The resulting solution was concentrated to ±2 ml and 25 ml of ether was added and the solution stirred for 5 minutes. The resulting pale yellow to orange-yellow precipitate was then filtered and washed with 3 X 10 ml portions of ether to remove all displaced DBA and excess ligand. The complex was then dissolved in the minimum of acetone and filtered through celite filter aid (Johns–Manville) to remove palladium metal, giving a bright, clear, yellow to red solution, which was concentrated as before and 25 ml ether added. The precipitate was allowed to settle and the solution decanted. The complex was then dried under a stream of nitrogen and finally under vacuum (0.1 mm Hg) at room temperature. Yields were high being between 65 and 95%. The complexes can be recrystallized from tetrahydrofuran–ether or dichloromethane–ether to give pure, crystalline material. Analytical data, microanalyses and I.R., are given in Table I.

The complex where olefin = dmf, R = *p*-CH_3O-(C_6H_4) R′ = H was prepared as above except that on formation it immediately precipitates from solution as an orange-brown solid which was filtered and washed with 3 X 15 ml portions of acetone and 2 X 10 ml portions of ether and then dried under nitrogen and finally under vacuum. The resulting complex was too insoluble to allow recrystallization.

The complex where olefin = def, R = *p*-CH_3O-(C_6H_4)-R′ = H was prepared in the same way as previous complexes. However, during the preparation the complex partially precipitated as dark red-black crystals. The acetone solution was concentrated to approximately 5 ml and the crystals filtered and then washed with 3 X 20 ml portions of ether. To purify the complex it was dissolved in dichloromethane filtered through celite and then concentrated to ±10 ml and 40 ml of ether was added. The solution was then stirred for five minutes, the crystals were allowed to settle and the solution decanted. The complex was dried as before.

Complexes where olefin = dmf, R = tBu R′ = H, R = $[(CH_3)_2CH]_2CH$– R′ = N and olefin = def, R = tBu R′ = H owing to their solubility and lability could not be prepared according to the above procedures. Two methods have been employed to prepare the complexes where R = tBu R′ = H.

Method 1: An acetone (10 ml) suspension of 1.0 mmol of Pd(0) (either as $Pd(DBA)_2$ or $Pd_2(DBA)_3{\cdot}CHCl_3$) was stirred under nitrogen with 1.05 mmol of olefin and 1.10 mmol of DAB at room temperature for 48 hours to give a deep red black homogeneous solution. The solution was filtered through celite to give a clear red solution which was evaporated to dryness. 7 ml of ethanol was added to the resulting orange solid and the solution was stirred for 10 minutes to give a red solution and yellow solid (displaced DBA). The reaction mixture was then placed at –30 °C for two days and afterwards rapidly filtered cold. The yellow solid thus obtained was washed with 2 X 1 ml portions of cold ethanol and the washings added to the filtrate which was then evaporated to dryness giving a bright orange solid. The solid was then washed with 4 X 20 ml portions of hexane and dried under vacuum (0.1 mm Hg). Pure, crystalline complex may be obtained by recrystallising from tetrahydrofurane–hexane. Yields of approximately 90% were obtained.

Method 2: An acetone (7 ml) suspension of 1.0 mmol of Pd(0) (as $Pd_3(TTAA)_3$) was stirred under nitrogen with 1.05 mmol of olefin and 1.10 mmol of DAB at room temperature for 5 days to give an orange-red solution and yellow-brown precipitate (displaced TTAA). The solution was filtered and the solid washed with 2 X 3 ml portions of ethanol. The combined washings and filtrate were then evaporated to dryness to give a yellow-orange solid. The solid was then stirred for 10 min in 10 ml of ethanol, resulting in a red solution and a yellow precipitate. The reaction mixture was placed at –30 °C for 2 days and filtered cold. The yellow solid was washed with 2 X 2 ml portions of cold ethanol. The combined washings and filtrate were then evaporated to dryness. The orange solid was then dissolved in tetrahydrofuran, filtered through celite concentrated and 40 ml hexane was added. After allowing the orange crystals to settle the solution was decanted. The crystals were washed, 2 X 10 ml hexane, and then dried. Yields were approximately 90%.

Only method 1 was used to prepare (dmf) $Pd[(CH_3)_2CH]_2CHN:CHCH:NCH[CH(CH_3)_2]_2$ as reaction was exceedingly slow, after three days stirring, when reaction appeared to have ceased, some 20% of the original starting complex was recovered unreacted. After the described work up a yield of approximately 60% of pure, crystalline red-orange complex (based on amount of starting complex consumed) was obtained.

Analytical and I.R. data for all the above complexes are given in Table I.

Reaction of p-*Cl(C*$_6$*H*$_4$*)N:CHCH:N-*p-*Cl(C*$_6$*H*$_4$*) with Pd(DBA)*$_3$*·CHCl*$_3$

1 mmol of $Pd_2(DBA)_3\cdot CHCl_3$ was dissolved in 20 ml CH_2Cl_2 and 1.1 mmol *p*-$Cl(C_6H_4)N:CHCH:N$-*p*-$Cl(C_6H_4)$ was added with stirring. The colour of the solution went from deep purple to a red/brown and a red/brown solid precipitated. After stirring for $\frac{1}{2}$ hour the solution was concentrated to ±5 ml and 30 ml ether was added. The solution was filtered and the solid washed with 3 X 10 ml acetone and 2 X 10 ml ether. I.R. and microanalysis data are given in Table I. On the basis of microanalysis data this highly insoluble complex appears to be a dimer.

Reactions of (olefin)Pd(DAB) Complexes

Reaction of (olefin)Pd(tBuN:CHCH:NtBu) with triphenylphosphine. Olefin = TCNE, MAH and dmf. 0.5 mmol of (olefin)Pd(DAB) was stirred with 1.3 mmol of PPh_3 in 5 ml of acetone. The starting complex rapidly dissolved and reacted. After stirring for 30 minutes the acetone was evaporated under vacuum to ±2 ml, then 10 ml of ether was added and stirring continued for a further 30 minutes. On settling of the precipitate the ether was decanted leaving a yellow solid which was washed with 3 X 10 ml portions of ether. Yields were almost quantitative.

Reaction of (olefin)Pd(tBuN:CHCH:NtBu) (where olefin = dmf, def) with Excess Olefin

A slurry of 0.5 mmol of (olefin)Pd(tBuN:CHCH:tBuN) in 20 ml of ether (or hexane) was stirred for 4 hours with a large excess of the olefin. The colour of the original complex gradually faded to give a white precipitate and a pale orange solution. The solution was concentrated and the solid was separated by decanting the solution and was then washed with 3 X 10 ml ether and dried. For $[(dmf)_2Pd]_2DAB^{H}_{tBu}$, Found (calc.) %C = 43.20(42.65), %H = 5.72(5.47), %O = 26.38(26.73), %N = 2.91(2.93).

Reaction of (dmf)Pd(tBuN:CHCH:NtBu) with t-Butylisocyanide

0.5 mmol of (dmf)Pd(tBuN:CHCH:NtBu) was stirred with 2 mmol of t-butylisocyanide in 30 ml ether. A pale yellow solution was obtained which was filtered and concentrated to ±5 ml and 30 ml of hexane was added. The resulting off-white solid was filtered and washed with 2 X 10 portions of hexane. The yield of $(dmf)Pd(tBuNC)_2$ was almost quantitative.

Reaction of (olefin)Pd(tBuN:CHCH:NtBu) with Methylallyl Chloride. Olefin = dmf, def

0.5 mmol of (olefin)Pd(tBuN:CHCH:NtBu) was stirred with 1.0 mmol of methylallyl chloride in 20 ml of ether. After 1 hour the resulting pale yellow solution was filtered (G4 frit) and concentrated under vacuum to ±3 ml and 20 ml hexane was added. The resulting white solid was filtered and washed with 2 X 10 ml hexane, yielding 95% of [(methylallyl)(chloride)Pd]$_2$DAB$^{H}_{tBu}$. For [(methylallyl)(chloride)Pd]$_2$DAB$^{H}_{tBu}$, Found (calc.) %C = 38.73(38.44), %H = 6.12(6.10), %N = 4.96(4.98), %Cl = 12.09(12.62); IR ν(Pd–Cl) = 269 cm^{-1} (s); ^{1}H NMR spectra in $CDCl_3$, 1.44 (s, 18 H, tBu), 2.10 (s, 6H, CH_3), 2.80 (s, 4H, allyl), 3.82 (s, 4H, allyl), 8.65 (broad s, 2H, imine).

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