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Novel $(R_2PC_2H_4PR_2)M^0$−COT Complexes (M = Pd, Pt) Having Semiaromatic η^2-COT or Dianionic η^2(1,4)-COT Ligands†

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The complexes $(R_2PC_2H_4PR_2)Pd(C_2H_4)$ (R = ^{i}Pr, ^{t}Bu) react with COT by displacement of the ethene ligand to afford the novel mononuclear complexes $(R_2PC_2H_4PR_2)Pd(\eta^2\text{-}C_8H_8)$ (R = ^{i}Pr (**1a**), ^{t}Bu (**1b**)). The COT ligand of **1a**,**b** is semiaromatic; i.e., it is planar with alternating C−C and C═C bonds as expected for the monoanion $[C_8H_8]^-$. Treatment of **1a**,**b** with $(R_2PC_2H_4PR_2)$Pd−alkene complexes generates the dinuclear derivatives $\{(R_2PC_2H_4PR_2)Pd\}_2(\mu\text{-}\eta^2,\eta^2\text{-}C_8H_8)$ (R = ^{i}Pr (**2a**), ^{t}Bu (**2b**)). The complexes **2a**,**b** are labile; elimination of the COT ligand from **2a** gives rise to homoleptic $Pd_2(\mu\text{-d}^i\text{ppe})_2$. Reaction of $(\text{d}^i\text{ppe})PtCl_2$ with $(\text{tmeda})_2Li_2$COT or displacement of the alkene ligands in $\{(\text{d}^i\text{ppe})Pt\}_2(\mu\text{-}\eta^2,\eta^2\text{-}C_8H_{12})$ (**4**) or $(\text{d}^i\text{ppe})Pt(C_2H_4)$ (**5**) by COT produces $(\text{d}^i\text{ppe})Pt(\eta^2\text{-}C_8H_8)$ (**6a**), which in the solid state also has a semiaromatic COT ligand. In solution, complex **6a** is in equilibrium with the novel isomeric form $(\text{d}^i\text{ppe})Pt^{II}\{\eta^2(1,4)\text{-}C_8H_8\}$ (**6b**). The complexes are characterized by IR, MS, and solution and solid-state NMR.

Introduction

Cyclooctatetraene complexes of Pd and Pt are rather scarce. $(C_8H_8)PtCl_2$[1] was reported in 1953, but in the meantime apparently only $\{\eta^4(1,2,5,6)\text{-}C_8H_8\}PdCl_2$[2] and $\{\mu\text{-}\eta^4(1,2,5,6)\text{:}\eta^4(3,4,7,8)\text{-}C_8H_8\}(PtMe_2)_2$[3] have been structurally characterized.[4] The yellow complexes $(\text{dppf})Pd^0(C_8H_8)$[5] and $(\text{dppf})Pt^0(C_8H_8)$[5b] and some related compounds have only been generated in solution. For all these $M^{0,II}$−COT complexes (M = Pd, Pt) an *olefinic* COT ligand with a tub-shaped conformation has either been confirmed crystallographically or appears to be most likely.

We recently observed that the structurally characterized dark violet Ni complexes $(R_2PC_2H_4PR_2)Ni(\eta^2\text{-}C_8H_8)$ (R = ^{i}Pr, ^{t}Bu)[6] display the unusual feature[7] of planar COT ligands with alternating C−C and C═C bonds. This property of the COT ring has been postulated for the $[\text{COT}]^-$ anion and is termed *semiaromatic*, as opposed to the olefinic character of neutral COT (tub-shaped conformation with alternating C−C and C═C bonds) and the aromatic dianion $[\text{COT}]^{2-}$ (planar geometry and equal bond distances).[8] The semiaromatic form of the COT ligand can clearly be distinguished from others not only by X-ray crystallography but also by the intense color of the complexes and the IR and NMR spectra. Treating the mononuclear complexes $(R_2PC_2H_4PR_2)Ni(\eta^2\text{-}C_8H_8)$ with $[(R_2PC_2H_4PR_2)Ni^0]$ generated in situ gives rise to the dinuclear compounds $\{(\text{d}^i\text{ppe})Ni\}_2\{\mu\text{-}\eta^4(1,2,5,6)\text{:}\eta^4(3,4,7,8)\text{-}C_8H_8\}$ (olefinic COT ligand) and $\{(\text{d}^t\text{bpe})Ni\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_8H_8)$ (semiaromatic COT ligand),[6] respectively.

We have previously characterized $(R_2PC_2H_4PR_2)M^0$−alkene (M = Pd, Pt),[9,10] complexes, which we expected to be suitable as starting materials for the synthesis of the heavier d^{10} homologues of the semiaromatic Ni−COT complexes. We now report on the mononuclear complexes $(R_2PC_2H_4PR_2)Pd(\eta^2\text{-}C_8H_8)$ (R = ^{i}Pr (**1a**), ^{t}Bu (**1b**)), which have semiaromatic COT ligands in the solid

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† Abbreviations: cod, 1,5-cyclooctadiene; COT, cyclooctatetraene; d^{i}ppe, $^iPr_2PC_2H_4P^iPr_2$, bis(diisopropylphosphino)ethane; d^{t}bpe, $^tBu_2PC_2H_4P^tBu_2$, bis(di-*tert*-butylphosphino)ethane; dppf = 1,1′-bis(diphenylphosphino)ferrocene; NQS, nonquaternary suppression.

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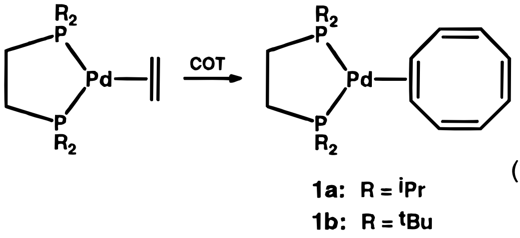
Table 1. IR (KBr) Resonances of the Semiaromatic η^2-COT Ligands of the Mononuclear (d^{i}ppe)M(η^2-C_8H_8) Complexes 1a (M = Pd) and 6a (M = Pt) and (d^{t}bpe)Pd(η^2-C_8H_8) (1b) and of Reference Compounds

compd	C=C$_{uncoord}$ (cm^{-1})	C=C$_{coord}$ (cm^{-1})
(d^{i}ppe)Ni(η^2-C_8H_8)[6]	1591 (s), 1533 (vs)	1485 (w)
1a	1602 (s), 1554 (vs)	1483 (w)
6a	1603 (s), 1545 (vs)	1465 (sh)
(d^{t}bpe)Ni(η^2-C_8H_8)[6]	1602 (s), 1553 (vs)	1490 (sh)
1b	1603 (s), 1556 (vs)	1489 (w)
Cp_2Ta(*n*-C_3H_7)(η^2-C_8H_8)[7]	1595 (s), 1515 (vs)	1470 (w)

state and in solution,[11] and on (d^{i}ppe)Pt(η^2-C_8H_8) (**6a**), which in the solid state has a semiaromatic COT ligand but in solution is in equilibrium with the isomeric form (d^{i}ppe)Pt^{II}{η^2(1,4)-C_8H_8} (**6b**).[10]

Results and Discussion

($R_2PC_2H_4PR_2$)Pd(η^2-C_8H_8) (R = ^{i}Pr (1a), ^{t}Bu (1b)). When 2−3 equiv of COT is added to the colorless ethereal solution of (d^{i}ppe)Pd(C_2H_4) or (d^{t}bpe)Pd(C_2H_4) at ambient temperature, the color changes to dark green. Upon cooling of the solution to −30 °C (**1a**) or within about 1 h at 20 °C (**1b**), violet crystals separate in >90% yield (eq 1). Although the crystals of **1a**,**b** appeared to be well-shaped they were not suitable for an X-ray structure analysis.



1a: R = ^{i}Pr
1b: R = ^{t}Bu

(1)

In the EI mass spectra the molecular ions of **1a** (*m*/*e* 472, 4%) and **1b** (528, 6%) fragment by loss of the COT ligand to produce the radical ions [(d^{i}ppe)Pd]$^+$ and [(d^{t}bpe)Pd]$^+$, respectively. Cleavage of a substituent R affords the even-electron ions [(^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr)Pd]$^+$ and [(^{t}Bu$_2$PC$_2$H$_4$P^{t}Bu)Pd]$^+$, which stabilize by Pd elimination into [^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr]$^+$ (base ion) and [^{t}Bu$_2$PC$_2$H$_4$P^{t}Bu]$^+$. The IR spectra of **1a**,**b** (Table 1) reveal a pattern of three bands for uncoordinated and coordinated C=C bonds, characteristic for a planar η^2-COT ligand.[6] The d^{i}ppe complex **1a** dissolves well in diethyl ether and THF, whereas the solubility of the d^{t}bpe derivative **1b** is significantly lower. In these dark green solutions small amounts of dinuclear **2a**,**b** are detectable (NMR), but the solutions still seem to be stable for at least several weeks. According to solution NMR, no fast exchange of the coordinated and uncoordinated COT occurs.

Solution and Solid-State CP-MAS NMR Spectra of 1a,b. The solution ^{31}P NMR spectra of **1a**,**b** show sharp singlets (−80 to 20 °C). In the solution ^{1}H and ^{13}C NMR spectra (20 °C) the COT ligand gives rise to single resonances (**1a**, δ_H 4.73, δ_C 108.2; **1b**, δ_H 4.74, δ_C 111.4) which for **1a** are split into triplets due to spin−spin coupling with the phosphorus atoms (Table 2). As compared to uncoordinated COT, these resonances are shifted to high field and the coupling ^1J(CH) is lowered to 151 Hz, but the changes are smaller than for the Ni analogues, consistent with a lower back-bonding ability of Pd^0 relative to that of Ni^0. The d^{i}ppe and d^{t}bpe signals are consistent with an apparent C_{2v} symmetry of the complexes on time average. When the temperature is lowered to −80 °C, the COT resonances of **1a** are slightly broadened so that the splittings due to ^{31}P are no longer resolved, and the COT resonances of **1b** are broadened to such an extent that the ^{13}C signal vanishes.

Table 2. Solution ^{1}H and ^{13}C NMR Data (COT Ligand) and ^{31}P NMR Data of Mononuclear 1a,b and 6a, of Dinuclear 2a,b, and of Reference Compounds[a]

	δ_H	δ_C	^1J(CH) (Hz)	δ_P
COT[6]	5.72	132.7	154.5	
Li_2COT[6]	5.73	87.5	144.7	
(d^{i}ppe)Ni(η^2-C_8H_8)[6]	4.62	103.4	149.7	81.7
(d^{i}ppe)Pd(η^2-C_8H_8) (**1a**)	4.73	108.2	151	67.3
	J(PH) 1.8[c]	*J*(PC) 3.1[c]		
(d^{i}ppe)Pt(η^2-C_8H_8) (**6a**)[b]	4.87[d]	102.3[d]	149	78.7
(d^{t}bpe)Ni(η^2-C_8H_8)[6]	4.50	106.5	148.8	93.0
(d^{t}bpe)Pd(η^2-C_8H_8) (**1b**)	4.74[e]	111.4[e]	151	84.2
{(d^{i}ppe)Pd}$_2$(μ-η^2,η^2-C_8H_8) (**2a**)	4.47[e]	94.5[d,e]	151	57.3
{(d^{t}bpe)Ni}$_2$(μ-η^2,η^2-C_8H_8)[6]	4.32	90.9	147.0	79.1
{(d^{t}bpe)Pd}$_2$(μ-η^2,η^2-C_8H_8) (**2b**)	4.44[e]	95.3[d,e]		77.4

[a] Solvent THF-d_8. Temperature 27 °C. [b] Temperature −80 °C (^{1}H, ^{31}P), −100 °C (^{13}C). [c] Averaged coupling (in hertz) for the fluctional structure. [d] Broad. [e] Couplings *J*(PH) and *J*(PC) are not observed.

The solid-state ^{31}P CP-MAS NMR spectra (25 °C) of **1a**,**b** display two signals which are attributed to an unresolved AB spin system (**1a**, δ_P 75.7, 74.6; **1b**, δ_P 92.5, 91.0). A first indication for the presence of a coupled spin system comes from the change of the sideband pattern with rotation frequency. The couplings *J*(PP) = 40 ± 5 Hz (**1a**) and 27 ± 5 Hz (**1b**) were determined by *J*-resolved 2D ^{31}P NMR spectroscopy. In the ^{13}C CP-MAS NMR spectrum of **1a** (25 °C), three partially resolved signals are detected for four PCH groups and five signals for eight Me groups (δ_C 22.4, 21.3, 20.4 (3-fold degenerate), 19.8, 19.4, 16.8; mean 20.1) of the d^{i}ppe ligand, whereas the two resonances expected for inequivalent PCH_2 are obscured. The COT ligand again gives rise to a *sharp* signal (δ_C 104.8). A NQS ^{13}C NMR experiment[12] provided evidence that the equivalence of the eight ^{13}C nuclei of the COT ligand results from fluxionality. In the ^{13}C CP-MAS NMR spectrum of **1b**, the d^{t}bpe signals of four inequivalent P*C*Me$_3$ (δ_C 37.2 (2-fold degenerate), 35.4, 34.9; mean 36.2) and two PCH_2 groups (δ_C 26.2, 24.5) are fairly well resolved but the four resonances expected for PC*Me$_3$* overlap. Here, the COT ligand gives rise to a *broad* signal (δ_C 106.5). Thus, although the d^{i}ppe and d^{t}bpe solid-state NMR signals of **1a**,**b** indicate that the complexes have C_1 symmetry, the COT ligands are still fluxional at ambient temperature. The very low symmetry of metal phosphane complexes apparent when

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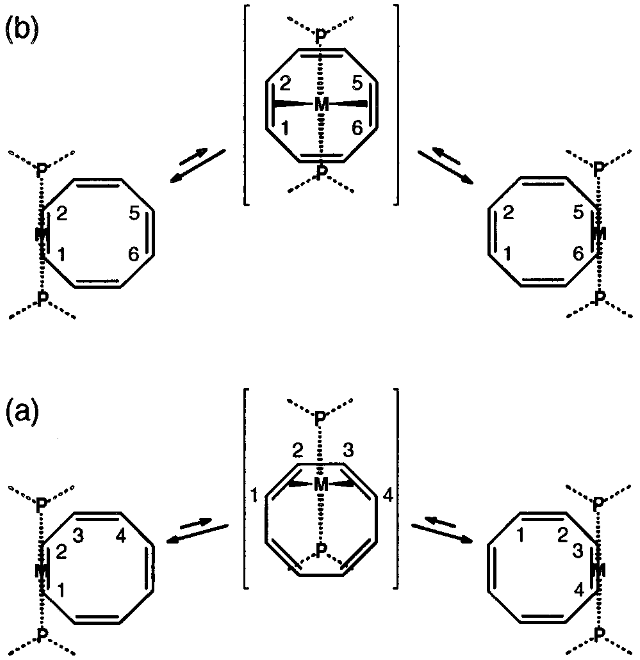

Figure 1. Suggested mechanism of the exchange of coordinated and uncoordinated COT C=C bonds in the ($R_2PC_2H_4PR_2$)M(η^2-COT) complexes **1a**,**b** (M = Pd) and **6a** (M = Pt): (a) low-energy process via a *T*-4 M^0−η^4(1−4)-C_8H_8 transition state; (b) presumed high-energy process via a *T*-4 M^0−η^4(1,2,5,6)-C_8H_8 transition state.

studied by solid-state NMR spectroscopy has been encountered before by us[6,28] and others.[13]

It is obvious from a qualitative examination of the NMR spectra that the exchange rate of the dynamic process of the d^{t}bpe derivative **1b** is markedly slower than for the d^{i}ppe derivative **1a**. This result implies that the transition state for fluxion is more hindered than the ground state. In the low-temperature ^{13}C CP-MAS NMR spectrum of **1b**, recorded at 85 K ($T_c \approx 190$ K), six separate COT signals are observed for the carbon atoms of three uncoordinated (δ_C 137.9, 126.1, 122.5, 117.6, 110.7, 108.7) and two signals for a coordinated C=C bond (δ_C 61.5, 60.3; mean value of all shifts, 105.7).

Hence, the solid-state NMR spectra of **1a**,**b** are in agreement with a η^2-coordinated COT ligand in the ground-state structure. This η^2-COT complex is highly fluxional even in the solid due to a rapid exchange of coordinated and noncoordinated C=C bonds.[9a,14] With regard to the mechanism of the exchange process we suggest that in solution the complexes pass through *T*-4 ($R_2PC_2H_4PR_2$)Pd{η^4(1−4)-C_8H_8} (low-energy route; Figure 1a) or *T*-4 ($R_2PC_2H_4PR_2$)Pd{η^4(1,2,5,6)-C_8H_8} transition states[15] (high-energy route; Figure 1b), whereas in the solid state merely the low-energy route (Figure 1a) appears to be likely because it involves the least motion of the COT ligand. Similar structural dynamics have been described for the Ni^0 derivatives.[6]

It follows from the close relationship between the mononuclear Pd^0−COT complexes **1a**,**b** and the structurally characterized Ni^0 homologues[6] that the electronic character of the COT ligand in **1a**,**b** can also be described as semiaromatic. The COT dynamics of **1a**,**b** are somewhat slower than for the Ni^0 derivatives for which the limiting ^{13}C CP-MAS NMR spectra of the static structures are not observable at 85 K. The reason for this might be 2-fold: First, the energy barrier to attain the *T*-4 M^0-η^4(1−4)-C_8H_8 transition state in Figure 1a is expected to be larger for Pd than for Ni as an intrinsic property of the metals. Second, due to the lower back-bonding ability of Pd^0 relative to Ni^0 the η^2-COT ligand in **1a**,**b** is possibly not strictly planar so that some flexing of the ring has to be overcome. All in all, the extraordinary fluxionality, among other features, represents a characteristic property of a semiaromatic η^2-COT ligand, as opposed to an olefinic η^2-COT ligand for which a static coordination is expected.[16,17]

{($R_2PC_2H_4PR_2$)Pd}$_2$(μ-η^2,η^2-C_8H_8) (R = ^{i}Pr (2a), ^{t}Bu (2b)). In an attempt to synthesize dinuclear Pd−COT complexes that are analogous to the aforementioned Ni−COT complexes, mononuclear **1a**,**b** have been treated with [($R_2PC_2H_4PR_2$)Pd^0] (R = ^{i}Pr, ^{t}Bu) or lithium metal.

When the dark green THF-d_8 solution of **1a** is combined with the equimolar amount of (d^{i}ppe)Pd(C_2H_4), the ^{31}P NMR spectrum (27 °C) shows the singlets of nonreacted amounts of **1a** (δ_P 67.3) and (d^{i}ppe)Pd(C_2H_4) (δ_P 62.7) and a new singlet which is attributed to about 10% of dinuclear **2a** (δ_P 57.3). Heating the solution to 50 °C for 90 min will increase the amount of **2a** to about 25%, but the signals of residual **1a** and (d^{i}ppe)Pd(C_2H_4) are still present; in addition, the singlet of homoleptic Pd_2(μ-d^{i}ppe)$_2$ (δ_P 33.7)[18] is observed. In a similar experiment equimolar amounts of mononuclear **1a** were reacted with (d^{i}ppe)-Pd^{II}(η^1-2-MeC_3H_4)$_2$,[19] which is converted into (d^{i}ppe)-Pd^0{η^2-CH_2=C(Me)C_2H_4C(Me)=CH_2} upon warming above −40 °C. The latter is more reactive than (d^{i}ppe)-Pd(C_2H_4) and presently the best source for the [(d^{i}ppe)-Pd^0] moiety.[18] When the violet suspension is warmed from −78 to 20 °C, a homogeneous red solution is obtained. Now the ^{31}P NMR spectrum displays the singlets of a residual amount of **1a** and of increased amounts of dinuclear **2a** (46%) and Pd_2(μ-d^{i}ppe)$_2$ (6%). After addition of a further 1 equiv of (d^{i}ppe)Pd(η^1-2-MeC_3H_4)$_2$ to the reaction solution (−78/20 °C), the signal of **1a** shrinks further but does not vanish, whereas the signal of **2a** is seemingly unchanged and the signal of Pd_2(d^{i}ppe)$_2$ increases in intensity. At this stage a mixture of about 29% of **1a**, 55% of **2a**, and 16% of Pd_2(μ-d^{i}ppe)$_2$ is present (^{31}P NMR). In a third experiment we have reacted **1a** with lithium metal in diethyl ether (20 °C, 15 min) in order to remove a 0.5 equiv of COT in the form of Li_2COT. However, in addition to signals which are due to extensive decomposition of **1a**, the ^{1}H,

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[14] The fast bond exchange in **1a**,**b** is in contrast to the static structure of complexes ($R_2PC_2H_4PR_2$)Pd(C_2H_4) (R = ^{i}Pr, ^{t}Bu), for which *no rotation* of the ethene ligand *about the bond axis* to Pd^0 is observed (NMR).

[15] To the best of our knowledge for all isolated ($R_2PC_2H_4PR_2$)Pd^0−alkene complexes with multifunctional alkene ligands the geometry is *TP*-3 and not *T*-4.[9a] It is thus assumed that *T*-4-Pd^0 coordination is attained only in a *transition state* and not in an intermediate.

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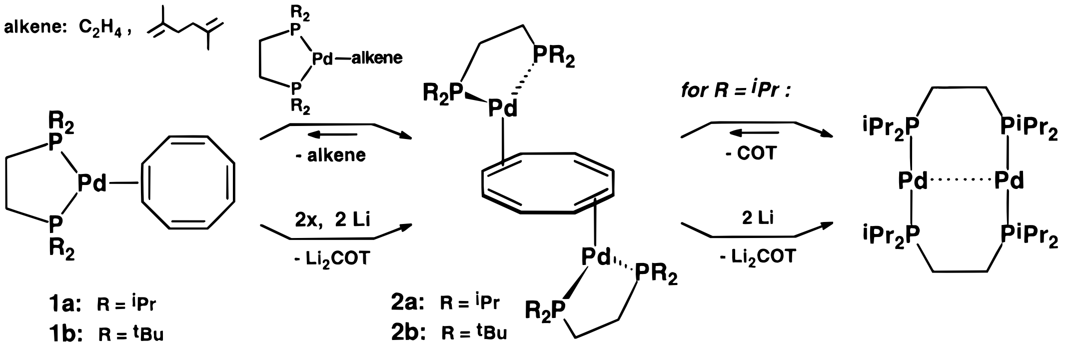
Scheme 1



^{13}C, and ^{31}P NMR spectra only show the signals of Li$_2$COT and Pd$_2$(μ-d^{i}ppe)$_2$.

When the solution of **1b** (δ_P 84.2) in THF-d_8 is mixed with (d^{t}bpe)Pd(C$_2$H$_4$) (δ_P 84.8) at 20 °C, a new signal arises which is attributed to 7% of **2b** (δ_P 77.4). Heating the solution to 50 °C for 90 min increases the amount of **2b** to about 15% but also causes the formation of byproducts (^{31}P NMR). Thereby the color changes from dark green to red brown. When **1b** is treated with an equimolar amount of (d^{t}bpe)Pd(η^1-2-MeC$_3$H$_4$)$_2$ and the temperature is raised from −78 to 20 °C, a ruby red solution results which according to the ^{31}P NMR spectrum consists of a mixture of **1b** (25%) and **2b** (75%), again with significant amounts of byproducts. The reaction of **1b** with lithium in diethyl ether at 20 °C (which is markedly slower than for **1a**) affords after 1 h about 15% and after 6 h about 53% of **2b**, but large amounts of byproducts arise here as well. The byproducts in these reactions have not been identified, but a homoleptic complex "Pd$_2$(d^{t}bpe)$_2$" does not appear to be among these.

These observations are rationalized by the reactions of Scheme 1. Obviously, the dinuclear complexes **2a**,**b** are less readily formed than the corresponding mononuclear complexes **1a**,**b** (eq 1), which is explained by the relatively poor back-bonding ability of Pd^0 combined with the charge accumulation at the COT ligand. Thus, even the most reactive [(R$_2$PC$_2$H$_4$PR$_2$)Pd^0] sources did not allow a gentle and clean formation of **2a**,**b**. Furthermore, **2a**,**b** are apparently labile. Complex **2a** is susceptible to elimination of the central COT ligand to afford COT-free Pd$_2$(μ-d^{i}ppe)$_2$, presumably in an equilibrium reaction. The formation of the latter complex is also facilitated by the reaction of either **1a** or **2a** with lithium, eliminating the COT ligand in form of Li$_2$COT. A corresponding formation of COT-free "Pd$_2$(d^{t}bpe)$_2$" from **2b** is apparently not feasible because of steric reasons.

Although complexes **2a**,**b** have not been isolated pure, they have been spectroscopically characterized. In the IR spectrum the complexes exhibit a strong COT ring-stretching mode at 1462 (**2a**) or 1477 cm^{-1} (**2b**), which compares well with the corresponding band of the Ni analogue to **2b**, {(d^{t}bpe)Ni}$_2${μ-η^2(1,2):η^2(5,6)-C$_8$H$_8$} (1476 cm^{-1}).[6] In the solution NMR spectra of **2a**,**b** at 27 °C, single ^{1}H and ^{13}C COT resonances are observed (Table 2).[20] The resonances are relatively sharp for **2a** but rather broad for **2b**. The signals indicate a rapid rotation of the COT ligands which, however, for **2b** is markedly slower than for the Ni derivative, as observed for the mononuclear complexes. For the COT ligand in **2a** the coupling ^1J(CH) = 151 Hz is the same as for mononuclear **1a**,**b**. For **2a**,**b** the COT ^{1}H resonances are about 0.3 ppm and the ^{13}C resonances are about 15 ppm to higher field than for mononuclear **1a**,**b**, which correlates with an increased charge at the COT ligand. Both ^{1}H and ^{13}C resonances, however, are downfield from those of the dinuclear Ni derivative, corresponding to weaker back-bonding from Pd^0 as compared with Ni^0. Similar shifts are observed for the ^{31}P resonances, which for dinuclear **2a**,**b** are 7−10 ppm to higher field than for mononuclear **1a**,**b**, indicating that the COT ligand acceptor strength toward each [(R$_2$PC$_2$H$_4$PR$_2$)Pd^0] fragment is weaker for the 2-fold than for the singly coordinated COT.

On the basis of the intense red color of **2a**,**b**, the IR and NMR resonances, and the dynamic COT coordination, all of which correspond to the features of the aforementioned binuclear and structurally characterized (d^{t}bpe)Ni−COT derivative, we conclude that the Pd complexes **2a**,**b** also display semiaromatic COT ligands as depicted in Scheme 1.

(d^{i}ppe)Pt(η^2-C$_8$H$_{12}$) (3), {(d^{i}ppe)Pt}$_2$(μ-η^2,η^2-C$_8$H$_{12}$) (4), and (d^{i}ppe)Pt(C$_2$H$_4$) (5). As part of our study of homologous series of Ni^0, Pd^0, and Pt^0 compounds, we have synthesized some new (d^{i}ppe)Pt−cod and ethene complexes which could serve both as starting complexes for the synthesis of a corresponding (d^{i}ppe)Pt−COT complex and as reference compounds.

When a suspension of Pt(cod)$_2$[21] in diethyl ether is stirred with 1 equiv of d^{i}ppe at 20 °C, the solid dissolves almost completely within a few minutes. The ^{31}P NMR spectrum of a colorless THF-d_8 solution (27 °C) displays two singlets, both flanked by ^{195}Pt satellites (I = $^1/_2$, 33.8%). The signal of the major component (90%) at δ_P 81.3 (^1J(^{195}PtP) = 2990 Hz) is attributed to complex **3**, whereas the signal of the minor component (10%) corresponds to the T-4 Pt^0 complex Pt(d^{i}ppe)$_2$ (δ_P 43.9, ^1J(^{195}PtP) = 3584 Hz). All attempts to isolate complex **3** in a pure form have failed. However, when the reaction solutions are kept at 20 °C for several days, fine pale yellow crystals of the dinuclear complex **4** (mp 166 °C dec) separate in 50% yield (Scheme 2).

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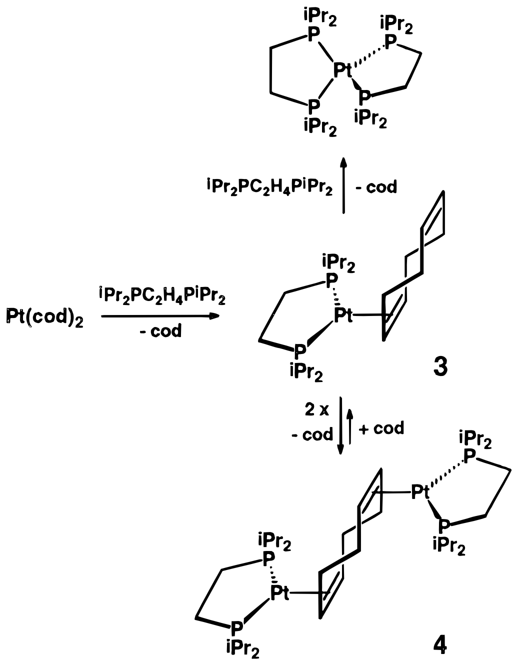
[20] ^{1}H NMR (200 MHz, 27 °C) of **2b**, d^{t}bpe ligands: δ_H 1.78 (m, 8H, PCH$_2$), 1.24 (m, 72H, CH$_3$).

[21] (a) Müller, J.; Göser, P. *Angew. Chem.* **1967**, *79*, 380; *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 364. (b) Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 271. (c) Herberich, G. E.; Hessner, B. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34*, 638. (d) Crascall, L. E.; Spencer, J. L. *Inorg. Synth.* **1990**, *28*, 126.

Scheme 2

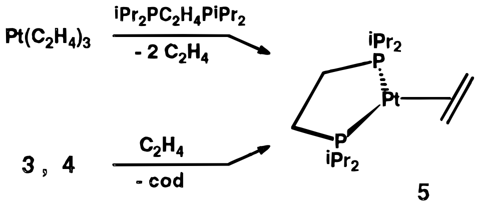


Complex **4** dissolves only poorly in the usual organic solvents. In the mass spectrum (220 °C) the molecular ion (*m*/*e* 1022) is observed which fragments by various routes. Cleavage of (d^{i}ppe)Pt(cod) from the molecular ion produces the base ion [(d^{i}ppe)Pt]$^+$ (457). The latter is also formed from [(d^{i}ppe)Pt(cod)]$^+$ (565) by elimination of the cod ligand. In addition, the molecular ion may first extrude the bridging cod ligand to afford the dinuclear ion [(d^{i}ppe)$_2$Pt$_2$]$^+$ (914), which subsequently splits into the base ion [(d^{i}ppe)Pt]$^+$.

In the ^{1}H NMR spectrum (300 MHz, THF-d_8, 27 °C) of **4** the cod ligand gives rise to a signal at δ_H 2.88 for the olefinic protons, which is split by couplings to ^{31}P and ^{195}Pt ($^2J(^{195}PtH) = 69$ Hz), and to two multiplets for inequivalent methylene protons $-CH_aH_b-$ (δ_H 2.65, 1.72). In the ^{13}C NMR spectrum (75.5 MHz) the olefinic C atoms of the cod ligand resonate at δ_C 52.2 ($^1J(^{195}PtC) = 252$ Hz) and the methylene C atoms at δ_C 41.4. In the ^{1}H and ^{13}C NMR spectra for the d^{i}ppe ligands four signals for two pairs of diastereotopic Me groups and two resonances for PCHMe$_2$ (unresolved for ^{1}H) are observed. The PCH$_a$H$_b$− moieties afford a single methylene ^{13}C resonance while the two expected ^{1}H resonances are unresolved. The ^{31}P NMR signal of **4** at δ_P 82.0 lies to slightly lower field than that of **3** and $^1J(^{195}PtP) = 3000$ Hz is of a magnitude typical for a Pt^0 complex.[22] The ^{1}H, ^{13}C, and ^{31}P NMR spectra of **4** are in agreement with a C_{2h} (or C_{2v}) symmetrical dinuclear complex in which two *TP*-3 (d^{i}ppe)Pt^0 centers are bridged by a μ-η^2,η^2-cod ligand.

When cod is added to a solution of dinuclear **4**, in the ^{31}P NMR spectrum the sharp signal of **3** is observed in addition to that of **4**. The ^{1}H NMR spectrum displays new signals for the cod ligand in **3** (δ_H 4.30 (=CH), 2.35 (CH$_2$)) and uncoordinated cod (δ_H 5.48 (=CH), 2.40 (CH$_2$)), besides the cod ligand signals of **4** and the overlapping d^{i}ppe signals of **3** and **4**. The =CH chemical shift of **3** (4.30) is in the region of an average (4.18) between a coordinated (2.88, in **4**) and an uncoordinated cod double bond (5.48, in cod), suggesting that a fluxional η^2-cod ligand is present. We thus assume that nonisolable **3** is the mononuclear derivative of **4** in which a η^2-C_8H_{12} ligand is coordinated to the *TP*-3 (d-^{i}ppe)Pt^0 center. The ^{1}H and ^{31}P NMR spectra indicate furthermore that mononuclear **3** is in slow equilibrium with dinuclear **4** and cod (Scheme 2). Presumably, dinuclear **4** separates from the reaction solution due to its lower solubility. Complexes **3** and **4** are closely related to (d^{i}ppe)Pd(η^2-cod) (not isolated) and {(d^{i}ppe)-Pd}$_2$(μ-η^2,η^2-cod)[9a] as well as (d^{t}bpe)Ni(η^2-cod) and {(d-^{t}bpe)Pd}$_2$(μ-η^2,η^2-cod).[23]

Scheme 3



The system is markedly simplified when ethene is added—Pt(cod)$_2$ suspended in diethyl ether dissolves to form Pt(C$_2$H$_4$)$_3$.[21b] After addition of 1 equiv of d^{i}ppe, yellow cubes of **5** crystallize at −30/−78 °C in 90% yield. Complex **5** is also obtained when ethene is added to solutions/suspensions of **3** or **4**, demonstrating that the cod ligand in these complexes is readily displaced by ethene (Scheme 3).

Complex **5** (mp 60 °C dec) is stable indefinitely at 20 °C. The IR spectrum (KBr) of **5** reveals for the ethene ligand a =C−H stretching band at 3020 cm^{-1} and a =C−H deformation band at 1120 cm^{-1}, whereas the C=C stretching band is obscured by phosphane bands. In the EI mass spectrum (70 °C) the molecular ion (*m*/*e* 485) is observed. Cleavage of the ethene ligand affords the base ion [(d^{i}ppe)Pt]$^+$ (457). In the ^{1}H NMR spectrum (200 MHz, THF-d_8, 27 °C) of **5** the ethene ligand resonates at δ_H 1.63 ($^2J(^{195}PtH) = 58$ Hz). For the d-^{i}ppe ligand in the ^{1}H and ^{13}C NMR spectra one PCH$_2$ and one P*CH*Me$_2$ signal and two signals for diastereotopic methyl groups PCH*Me*$_2$ are observed. In the ^{31}P NMR spectrum a singlet is observed at δ_P 83.1 [$^1J(^{195}PtP) = 3164$ Hz].

(d^{i}ppe)Pt(η^2-C$_8$H$_8$) (6a) and (d^{i}ppe)Pt^{II}{η^2(1,4)-C$_8$H$_8$} (6b). When a suspension of equimolar amounts of (d^{i}ppe)PtCl$_2$ and (tmeda)$_2$Li$_2$(C$_8$H$_8$) in a mixture of THF and COT is stirred at 20 °C for several hours, a dark brown reaction mixture results. After evaporation of the solvent under vacuum and extraction of the residue with toluene, dark red intergrown crystals of **6a** separate at −78 °C in 82% yield (Scheme 4). Complex **6a** is also obtained by displacement of the olefinic ligands in **3**−**5** by 1 equiv of COT (20 °C). The crystals of **6a** were not suitable for an X-ray structure analysis.

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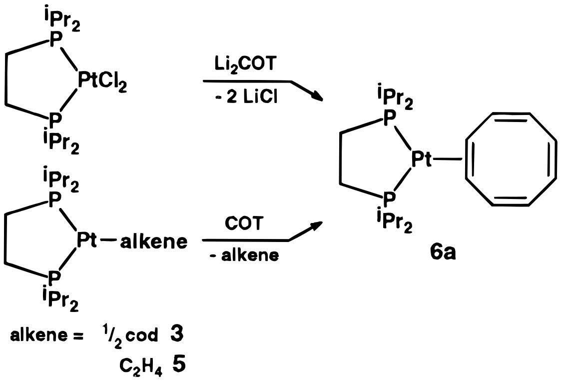
(22) Generally,[22a] bis(phosphane)platinum(0) complexes display couplings $^1J(^{195}PtP)$ of about 3000−3500 Hz (cf. **4**, 3000 Hz, and **5**, 3164 Hz), whereas for bis(phosphane)platinum(II) complexes smaller couplings of 1800−2500 Hz are observed (cf. (d^{i}ppe)Pt(η^1,η^1-C$_4$H$_6$), 1816 Hz; (Me$_2$PC$_2$H$_4$PMe$_2$)Pt(η^1,η^1-C$_8$H$_{12}$), 1831 Hz).[22b] (a) Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Springer: Berlin, 1979. (b) Benn, R.; Jolly, P. W.; Joswig, T.; Mynott, R.; Schick, K.-P. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1986**, *41*, 680. Benn, R.; Betz, P.; Goddard, R.; Jolly, P. W.; Kokel, N.; Krüger, C.; Topalovic, I. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1991**, *46*, 1395.

(23) Pörschke, K.-R.; Pluta, C.; Proft, B.; Lutz, F.; Krüger, C. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1993**, *48*, 608.

Scheme 4



Solid **6a** (mp 135 °C) is stable indefinitely in an inert atmosphere at ambient temperature. The complex dissolves poorly in diethyl ether or pentane (20 °C) but well in THF or toluene, even at low temperature. In solution, **6a** is in equilibrium with isomer **6b** as shown below. The red brown solutions may be kept unchanged at 20 °C for several weeks. In the IR spectrum (KBr), solid **6a** displays a pattern of three bands for uncoordinated and coordinated C=C bonds (Table 1) which appears to be characteristic for a semiaromatic η^2-COT ligand.[6] In the EI mass spectrum (125 °C) the molecular ion (*m/e* 561) is observed which fragments by loss of the COT ligand to produce the base ion [(d^{i}ppe)Pt]$^+$.

Solid-State NMR Spectra of 6a. In the ^{31}P CP-MAS NMR spectrum (24 °C) of **6a** two signals are observed at δ_P 77.8 ($^1J(^{195}$PtP) = 3244 Hz) and δ_P 75.2 ($^1J(^{195}$PtP) = 3260 Hz). The magnitude of the ^{195}Pt spin–spin couplings indicates the presence of a Pt^0 complex.[22] The coupling ^2J(PP) = 27 ± 5 Hz was not resolved but was determined by *J*-resolved 2D ^{31}P NMR spectroscopy (Figure 2).

In the ^{13}C CP MAS NMR spectrum (24 °C) of **6a**, for the d^{i}ppe ligand some signal overlap occurs and three signals are observed for four PCH groups (δ_C 29.7–27.4) and five signals for eight Me groups (δ_C 22.1 (2C), 21.3 (3C), 19.5 (1C), 19.0 (1C), 16.8 (1C)) as well as two signals for inequivalent PCH$_2$ groups (δ_C 25.3, 23.5). The COT ligand gives rise to a sharp singlet at δ_C 102.6. The d^{i}ppe ligand solid-state ^{13}C and ^{31}P NMR signals of **6a** (24 °C) indicate C_1 symmetry, but the coordination of the COT ligand is obviously fluxional, similar to **1a**,**b**. The fluxionality of the COT ligand has been confirmed by NQS ^{13}C NMR.[12] When the temperature is lowered to 85 K ($T_c \approx$ 133 K), the COT signal is split into three broad lines for uncoordinated C=C groups (δ_C 128.4, 118.8, and 109.4) and a fourth line for a coordinated C=C moiety at δ_C 49.3 (arithmetic mean of all four signals: 101.5). The spectrum resembles that of **1b** for which, however, eight signals are observed at this temperature. Thus, it appears that the exchange rate of the COT ligand in the (d^{i}ppe)Pt^0 complex **6a** is somewhat lower than for the (d^{i}ppe)Pd^0 homologue **1a** but greater than for the (d^{t}bpe)Pd^0 derivative **1b**.

In conclusion, both the solid-state NMR spectra and the IR spectrum of **6a** (the only isomer detected in the solid state) are in full agreement with the presence of a semiaromatic η^2-COT ligand which is coordinated to a *TP*-3 Pt^0 center.

Solution NMR Spectra. In solution (THF-d_8 or toluene-d_8) complex **6a** is in equilibrium with an isomer **6b** (eq 2). The solution ^{1}H, ^{13}C, and ^{31}P NMR spectra are temperature-dependent and are most conveniently described by starting with the low-temperature ^{31}P NMR spectrum.

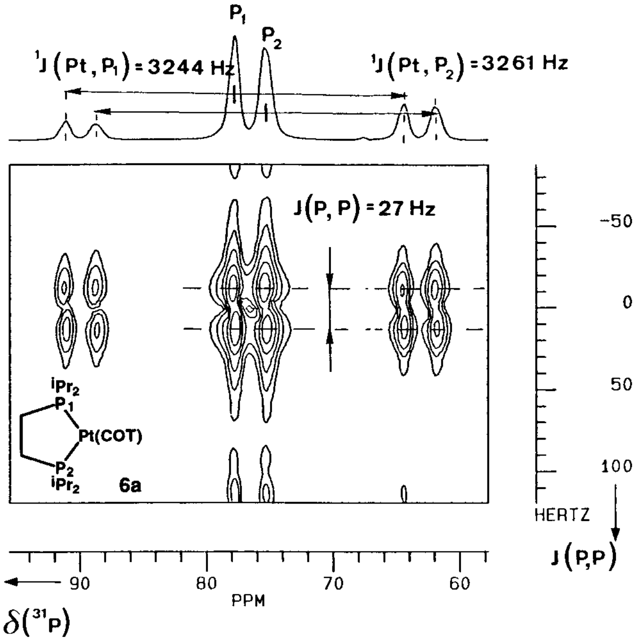
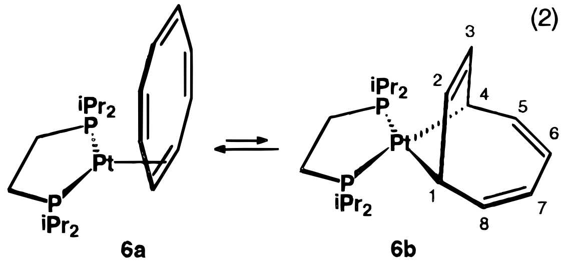


Figure 2. Isotropic part of the *J*-resolved 2D ^{31}P CP-MAS NMR spectrum of **6a**. The inequivalent ^{31}P atoms of the d^{i}ppe ligand give rise to an AB spin system with *J*(PP) = 27 ± 5 Hz, detected in the F1 dimension. The slightly different couplings $J(^{195}$PtP$_1)$ and $J(^{195}$PtP$_2)$ are observed in the F2 dimension.



(2)

The 121 MHz ^{31}P NMR spectrum (−80 °C) of a THF-d_8 solution of **6a** displays two sharp singlets at δ_P 78.7 (**6a**) and δ_P 67.2 (**6b**) (relative intensities 1:2) with ^{195}Pt satellites. The relatively large coupling $^1J(^{195}$PtP) = 3271 Hz of **6a** is compatible with a Pt^0 complex, whereas for **6b** the smaller coupling $^1J(^{195}$PtP) = 2238 Hz is indicative of a Pt^{II} complex.[22]

In the 300 MHz ^{1}H NMR spectrum (−80 °C) five (broad) signals are observed for COT ligands of which the signal at δ_H 4.87 (relative intensity 2) is assigned to isomer **6a** and the signals at δ_H 6.53, 5.53, 5.13, and 3.65 (mean 5.21; relative intensities 1:1:1:1) are attributed to isomer **6b**. The assignment has been verified by a ^{1}H COSY NMR spectrum.[24] In the solution ^{13}C NMR spectrum (75.5 MHz, −100 °C) isomer **6a** gives rise to a broad COT signal at δ_C 102.3. The COT ligand of **6b** displays four sharp signals at δ_C 149.1, 133.4, 123.3, and 41.7 (mean 111.9). ^{195}Pt satellites are observed only for the signal at δ_C 41.7 ($^1J(^{195}$PtC) = 456

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[24] Derome, A. E. *Modern NMR Techniques for Chemical Research*, Pergamon: Oxford, U.K., 1987.

Hz). Furthermore, two sets of d^{i}ppe ^{1}H and ^{13}C NMR signals in the intensity ratio 1:2 arise from the d^{i}ppe ligands of complex isomers **6a**,**b**. The COT ^{1}H and ^{13}C resonances of **6a** are at markedly higher field ($\Delta\delta_H$ = 0.35 ppm, $\Delta\delta_C$ = 9.6 ppm) than those of **6b** (mean values).

The solution low-temperature ^{1}H, ^{13}C, and ^{31}P NMR data assigned to isomer **6a** are very similar to those of the solid-state NMR spectra. As in the solid state, the COT ligand is fluxional in solution, and it is suggested that the exchange of the coordinated and the uncoordinated C═C bonds proceeds by the mechanisms depicted in Figure 1.

The ^{1}H, ^{13}C, and ^{31}P NMR data for isomer **6b** are compatible with an *SP*-4 Pt^{II} complex in which both d^{i}ppe and a cycloocta-2,5,7-triene-1,4-diyl ligand are coordinated at the Pt^{II} center. The resulting 9-platinabicyclo[4.2.1]nonatriene skeleton is presumably very rigid. The dianionic η^2(1,4)-C_8H_8 ligand is formally formed by oxidative 1,4-addition of a COT 1,3-diene subunit to the Pt^0 center and is isoelectronic with aromatic [COT]$^{2-}$. The complex is related to (d^{i}ppe)Pt{η^2(1,4)-C_4H_6}, the adduct of butadiene to the [(d^{i}ppe)Pt^0] fragment.[22b] A major difference between **6b** and (d^{i}ppe)Pt{η^2(1,4)-C_4H_6} is that in the latter the Pt^{II}{η^2-(1,4)-C_4H_6} coordination is static, whereas **6b** is in slow equilibrium with **6a**. The M{η^2(1,4)-C_8H_8} structural element of **6b** is novel for unsubstituted COT but has precedent for C_8F_8.[25]

When the temperature is raised to −20 °C, the ^{1}H and ^{13}C NMR COT and d^{i}ppe signals and the ^{31}P resonances of both isomers **6a**,**b** coalesce. In the ^{1}H (200 MHz) and ^{13}C NMR spectra of the COT ligand at ambient temperature a single sharp signal at δ_H 5.01 with resolved ^{195}Pt coupling satellites ($J(^{195}PtH) = 7$ Hz) and a very broad signal at δ_C 108.0 are observed. In the ^{31}P NMR spectrum a singlet at δ_P 73.3 is flanked by ^{195}Pt satellites ($^1J(^{195}PtP) = 2806$ Hz). Thus, at ambient temperature the isomers **6a**,**b** rapidly interchange their binding modes. Furthermore, as can be deduced from the COT ^{1}H and ^{13}C resonances, the ^{31}P resonance, and the coupling constant $^1J(^{195}PtP)$, all of which are weighted averages of **6a**,**b**, at ambient temperature the equilibrium according to eq 2 is shifted toward **6a**, whereas at low temperature it shifts toward **6b**. When COT (1 equiv) is added to such a solution, the COT signals of **6a**,**b** are unchanged and additional sharp signals of uncoordinated COT (Table 2) are observed. Consequently, on the NMR time scale uncoordinated COT is involved neither in the C═C bond exchange process of **6a** nor in the exchange **6a** $\rightleftharpoons$ **6b**. Similar spectra of **6a**,**b** are observed in toluene-d_8.

Conclusion

The novel mononuclear complexes ($R_2PC_2H_4PR_2$)M(η^2-C_8H_8) (M = Pd, R = ^{i}Pr (**1a**), ^{t}Bu (**1b**); M = Pt, R = ^{i}Pr (**6a**)) and the dinuclear complexes {($R_2PC_2H_4PR_2$)Pd}$_2$-(μ-η^2,η^2-C_8H_8) (R = ^{i}Pr (**2a**), ^{t}Bu (**2b**)) display semiaromatic COT ligands. Together with the previously isolated and structurally characterized Ni derivatives, these constitute a series of homologous mononuclear complexes for the Ni triad. It follows from this study that semiaromatic η^2-COT coordination is quite general for strongly back-bonding *TP*-3 16e d^{10} M^0 (M = Ni, Pd, Pt) centers.

For platinum it was also found that the formal Pt^0 complex **6a** in solution is in equilibrium with an *SP*-4 Pt^{II} isomer (d^{i}ppe)Pt{η^2(1,4)-C_8H_8} (**6b**). This novel type of COT coordination arises from oxidative 1,4-addition of a COT 1,3-diene subunit to the Pt^0 center. It appears to result from particularly strong back-bonding which increases in the series Pd^0 < Ni^0 < Pt^0 and leads to a formally bisanionic COT ligand.

Generally, it can be expected that strong metal back-bonding favors semiaromatic η^2-COT or η^2(1,4)-COT coordination. This situation is not confined to *TP*-3 16e d^{10} M^0 centers but is also found for 18e d^2 Ta^{II} in Cp_2-Ta(n-C_3H_7)(η^2-C_8H_8),[7] and it is furthermore expected for 18e d^6 Re^I and Os^{II}.[26]

Experimental Section

To exclude oxygen and moisture, all operations were conducted under an atmosphere of argon by standard Schlenk techniques. Pd(η^3-C_3H_5)$_2$,[27] Pd(η^3-2-MeC_3H_4)$_2$,[27] (d^{i}ppe)Pd(η^1-C_3H_5)$_2$,[9a] (d^{i}ppe)Pd(η^1-2-MeC_3H_4)$_2$,[19] (d^{i}ppe)Pd(C_2H_4),[9a] and Pt(cod)$_2$[21b,c] were prepared by published procedures. Microanalyses were performed by the Mikroanalytisches Labor Kolbe, Mülheim, Germany. THF-d_8 was used as the solvent for all solution NMR studies. ^{1}H NMR spectra (δ relative to TMS) were measured at 200, 300, and 400 MHz, ^{13}C NMR spectra (δ relative to TMS) at 50.3, 75.5, and 100.6 MHz, and ^{31}P NMR spectra (δ relative to external 85% aqueous H_3PO_4) at 81, 121.5, and 162 MHz on Bruker AC- and AM-200, AMX-300, and AMX-400 instruments. EI mass spectra (the data refer to ^{35}Cl, ^{106}Pd, and ^{195}Pt) were recorded at 70 eV on a Finnigan MAT 8200, and IR spectra, on a Nicolet 7199 FT-IR instrument. Solid-state ^{13}C and ^{31}P CP-MAS NMR spectra were recorded on a Bruker MSL-300 spectrometer; experimental conditions were as described.[28]

(^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$)PtCl$_2$.[10,29] The ochre suspension of $PtCl_2$ (2.66 g, 10.0 mmol) in water (50 mL) is stirred with d^{i}ppe (3.1 mL, 10.0 mmol) for 24 h. The resulting colorless precipitate is separated by filtration, washed with some ethanol, and dried under vacuum; yield 5.01 g (95%). EI-MS (200 °C) [*m/e* (%)]: 527 (M$^+$, 21), 492 ([(d^{i}ppe)PtCl]$^+$, 69), 449 ([(^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr)PtCl]$^+$, 95), 407 ([(^{i}Pr$_2$PC$_2$H$_4$PH)PtCl]$^+$, 38). Anal. Calcd for $C_{14}H_{32}Cl_2P_2Pt$ (528.3): C, 31.83; H, 6.10; Cl, 13.42; P, 11.72; Pt, 36.92. Found: C, 31.71; H, 6.02; Cl, 13.36; P, 11.69; Pt, 37.10.

Pt(^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$)$_2$. Stirring a mixture of Pt(cod)$_2$ (411 mg, 1.0 mmol) and d^{i}ppe (0.62 mL, 2.0 mmol) in diethyl ether (20 mL) affords a colorless solution. At −78 °C colorless prisms crystallize, which are separated from the mother liquor and dried under vacuum (20 °C): yield 575 mg (80%); mp 225 °C. EI-MS (140 °C) [*m/e* (%)]: 719 (M$^+$, 28), 677 ([M − C_3H_6, 100), 635 (M − 2C_3H_6, 37). ^{1}H NMR (400 MHz, 27 °C): δ 1.90 (m, 8H, PCH), 1.25 (m, 8H, PCH$_2$), 1.12, 1.10 (each m, 24H, diastereotopic PCH*Me*$_2$). ^{31}P NMR (81 MHz, 27 °C): δ 43.9,

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[26] It is expected that in Cp*Re(CO)$_2$(η^2-C_6H_6)[26a] and [(NH$_3$)$_5$Os-(η^2-C_6H_6)](CF$_3$SO$_3$)$_2$[26b,c] the benzene ligands can be displaced by COT to form the corresponding η^2-COT or η^2(1,4)-COT complexes. (a) van der Heijden, H.; Orpen, A. G.; Pasman, P. *J. Chem. Soc., Chem. Commun.* **1985**, 1576. (b) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 1883. Harman, W. D.; Gebhard, M.; Taube, H. *Inorg. Chem.* **1990**, *29*, 567. (c) Taube, H. *Pure Appl. Chem.* **1991**, *63*, 651.

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$^1J(^{195}PtP) = 3584$ Hz. Anal. Calcd for $C_{28}H_{64}P_4Pt$ (719.8): C, 46.72; H, 8.96; P, 17.21; Pt, 27.10. Found: C, 46.68; H, 9.41; P, 17.20; Pt, 26.69.

($^iPr_2PC_2H_4P^iPr_2$)Pd(η^2-C_8H_8) (1a). Addition of COT (0.3 mL, 2.7 mmol) to the colorless solution of (d^{i}ppe)Pd(C_2H_4) (397 mg, 1.0 mmol) in diethyl ether (20 mL) results in a dark green solution. Cooling to −30 °C affords violet crystals, which are freed from the mother liquor, washed with cold pentane, and dried under vacuum (20 °C): yield 440 mg (93%); mp 134 °C. IR (KBr): 2999, 660 cm^{-1} (=C−H) (C=C bands, see Table 1). EI-MS (80 °C) [*m/e* (%)]: 472 (M$^+$, 4), 368 ([(d^{i}ppe)Pd]$^+$, 32), 325 ([($^iPr_2PC_2H_4P^iPr$)Pd]$^+$, 11), 219 ([$^iPr_2PC_2H_4P^iPr$]$^+$, 100), 104 ([COT]$^+$, 91). ^{1}H NMR (300 MHz, 27 °C) (for C_8H_8, see Table 2): δ 2.12 (m, 4H, PCHMe$_2$), 1.71 (m, 4H, PCH$_2$), 1.16, 1.09 (each dd, 12H, diastereotopic CH$_3$), d^{i}ppe. ^{13}C NMR (75.5 MHz, 27 °C) (for C_8H_8, see Table 2): δ 26.8 (4C, PCHMe$_2$), 22.5 ("t", 2C, ^1J(PC) = 18.3 Hz, PCH$_2$), 20.1 ("d"), 19.2 ("s", each 4C, diastereotopic CH$_3$), d^{i}ppe. At −80 °C the ^{1}H and ^{13}C NMR spectra are almost unchanged but the COT resonances have lost their fine structure. ^{31}P NMR: 121.5 MHz, 27 °C, see Table 2; 162 MHz, −80 °C, δ 72.4. Anal. Calcd for $C_{22}H_{40}P_2Pd$ (472.9): C, 55.87; H, 8.53; P, 13.10; Pd, 22.50. Found: C, 55.84; H, 8.42; P, 12.96; Pd, 22.61.

($^tBu_2PC_2H_4P^tBu_2$)Pd(η^2-C_8H_8) (1b). Addition of COT (0.5 mL, 4.4 mmol) to the colorless solution of (d^{t}bpe)Pd(C_2H_4) (679 mg, 1.5 mmol) in diethyl ether (20 mL) results in a dark green solution. Upon standing for 1 h, violet crystals separate. After completion of the crystallization at −30 °C the crystals are isolated as described above: yield 745 mg (94%); mp 207 °C dec. IR (KBr): 2993, 669 cm^{-1} (=C−H) (C=C bands, see Table 1). EI-MS (110 °C) [*m/e* (%)]: 528 (M$^+$, 6), 424 ([(d^{t}bpe)Pd]$^+$, 59), 367 ([($^tBu_2PC_2H_4P^tBu$)Pd]$^+$, 60), 261 ([$^tBu_2PC_2H_4P^tBu$]$^+$, 93), 104 ([COT]$^+$, 53), 57 ([^{t}Bu]$^+$, 100). ^{1}H NMR (300 MHz, 27 °C) (for C_8H_8, see Table 2): δ 1.87 (m, 4H, PCH$_2$), 1.27 (m, 36H, CH$_3$), d^{t}bpe; at −80 °C (400 MHz) the C_8H_8 ^{1}H resonance is broad. ^{13}C NMR (75.5 MHz, 27 °C) (for C_8H_8, see Table 2): δ 35.8 ("s", 4C, PCMe$_3$), 30.7 ("t", 12C, CH$_3$), 24.4 ("t", 2C, PCH$_2$), d^{t}bpe; at −80 °C (100.6 MHz) the C_8H_8 ^{13}C resonance is very broad and has not been located unequivocally. ^{31}P NMR (121.5 MHz, 27 °C): see Table 2. Anal. Calcd for $C_{26}H_{48}P_2Pd$ (529.0): C, 59.03; H, 9.15; P, 11.71; Pd, 20.12. Found: C, 58.88; H, 9.27; P, 11.82; Pd, 20.19.

{($^iPr_2PC_2H_4P^iPr_2$)Pt}$_2$(μ-η^2,η^2-C_8H_{12}) (4). When a suspension of Pt(cod)$_2$ (411 mg, 1.0 mmol) and d^{i}ppe (0.31 mL, 1.0 mmol) in diethyl ether (20 mL) is stirred at 20 °C for a few minutes, a colorless solution results. Within about 1 week pale yellow prisms crystallize, which are freed from the mother liquor and dried under vacuum (20 °C): yield 510 mg (50%); mp 166 °C dec. EI-MS (220 °C) [*m/e* (%)]: 1022 (M$^+$, 3), 914 ([M − cod]$^+$, 22), 565 ([(d^{i}ppe)Pt(cod)]$^+$, 34), 457 ([(d^{i}ppe)Pt]$^+$, 100). ^{1}H NMR (300 MHz, 27 °C): δ 2.88 (m, 4H, ^3J(PH) = 7 Hz, ^2J(PtH) = 69 Hz, =CH), 2.65, 1.72 (each m, 4H, CH$_a$H$_b$), μ-cod; 2.08, 2.08 (each m, 4H, PCH and PC′H), 1.53 (m, 8H, PCH$_a$H$_b$), 1.11, 1.11, 1.06, 0.94 (each m, two pairs of diastereotopic Me), d^{i}ppe. ^{13}C NMR (75.5 MHz, 27 °C): δ 52.2 (4C, ^1J(CH) = 144 Hz, $^1J(^{195}PtC)$ = 252 Hz, C=C), 41.4 (4C, CH$_2$), μ-cod; 26.9, 26.5 (each 4C, PCH and PC′H), 25.1 (4C, PCH$_2$), 19.8, 19.7, 19.3, 19.0 (each 4C, two pairs of diastereotopic Me), d^{i}ppe. ^{31}P NMR (121.5 MHz, 27 °C): δ 82.0, $^1J(^{195}PtP)$ = 3000 Hz. Anal. Calcd for $C_{36}H_{76}P_4Pt_2$ (1023.1): C, 42.27; H, 7.49; P, 12.11; Pt, 38.14. Found: C, 42.19; H, 7.81; P, 12.02; Pt, 37.93.

($^iPr_2PC_2H_4P^iPr_2$)Pt(C_2H_4) (5). A suspension of Pt(cod)$_2$ (411 mg, 1.0 mmol) and d^{i}ppe (0.31 mL, 1.0 mmol) in diethyl ether (10 mL) is saturated with ethene gas and stirred at 20 °C. From the resulting solution yellow cubes crystallize at −78 °C. The product is separated from the mother liquor and dried under vacuum (20 °C): yield 437 mg (90%); mp 60 °C dec. EI-MS (70 °C) [*m/e* (%)]: 485 (M$^+$, 24), 457 ([(d^{i}ppe)Pt]$^+$, 100), 415 ([($^iPr_2PC_2H_4PH^iPr$)Pt]$^+$, 53). IR (KBr): 3020 (=C−H), 1120 cm^{-1} (C=C). ^{1}H NMR (200 MHz, 27 °C): δ 1.63 (m, 4H, $^2J(^{195}PtH)$ = 58 Hz), C_2H_4; 2.12 (m, 4H, PCH), 1.62 (m, 4H, PCH$_2$), 1.12, 1.02 (each dd, 12H, diastereotopic Me), d^{i}ppe. ^{13}C NMR (50.3 MHz, 27 °C): δ 27.0 (4C, PCH), 22.9 (2C, PCH$_2$), 20.2, 19.4 (each 4C, diastereotopic CH$_3$), d^{i}ppe; C_2H_4 is possibly overlapped by a THF signal ($\delta \approx 25$). ^{31}P NMR (81 MHz, 27 °C): δ 83.1, $^1J(^{195}PtP)$ = 3164 Hz. Anal. Calcd for $C_{16}H_{36}P_2Pt$ (485.5): C, 39.58; H, 7.47; P, 12.76; Pt, 40.18. Found: C, 39.75; H, 7.15; P, 12.88; Pt, 40.24.

($^iPr_2PC_2H_4P^iPr_2$)Pt(C_8H_8) (6a). To the suspension of (d-^{i}ppe)PtCl$_2$ (528 mg, 1.0 mmol) in THF (10 mL) and COT (5 mL) is added (20 °C) a THF suspension (5 mL) of (tmeda)$_2$Li$_2$(C_8H_8) (351 mg, 1.0 mmol). Upon stirring of the contents for 16 h, a dark brown mixture is obtained from which the volatile components are evaporated under vacuum. The residue is extracted with toluene, and the solution is concentrated to a volume of 10 mL. After the addition of diethyl ether (10 mL) dark red intergrown crystals are obtained at −78 °C. The product is separated from the mother liquor, washed twice with cold ether, and dried under vacuum (20 °C): yield 460 mg (82%); mp 135 °C. IR (KBr): 2997, 660 cm^{-1} (=C−H) (C=C bands, see Table 1). MS (125 °C) [*m/e* (%)]: 561 (M$^+$, 29), 457 ([(d^{i}ppe)Pt]$^+$, 100), 415 ([($^iPr_2PC_2H_4PH^iPr$)Pt]$^+$, 92), 373 ([($^iPrHPC_2H_4PH^iPr$)Pt]$^+$, 60). Anal. Calcd for $C_{22}H_{40}P_2Pt$ (561.6): C, 47.05; H, 7.18; P, 11.03; Pt, 34.74. Found: C, 47.14; H, 7.12; P, 10.88; Pt, 34.81.

Solution NMR of 6a,b. ^{1}H NMR (300 MHz, 32 °C): δ 5.01 (s, 8H, C_8H_8); 2.25 (m, 4H, PCH), 1.59 (m, 4H, PCH$_2$), 1.13, 1.06 (each dd, 12H, CH$_3$), d^{i}ppe. 80 or 200 MHz ^{1}H NMR, COT signal: $J(^{195}PtH)$, average value, 7 Hz. ^{13}C NMR (75.5 MHz, 32 °C): δ 108.0 (broad, C_8H_8); 26.9 (4C, PCH), 23.5 (2C, PCH$_2$), 19.6, 18.8 (each 4C, diastereotopic CH$_3$), d^{i}ppe. ^{31}P NMR (121 MHz, 32 °C): δ 73.3, ^1J(PtP) = 2807 Hz.

Isomer 6a. ^{1}H NMR (300 MHz, −100 °C): δ 4.87 (C_8H_8), ≈2.2 (obscured, PCH), 1.64 (PCH$_2$), ≈1.1, 0.87 (broad, diastereotopic CH$_3$), d^{i}ppe. ^{13}C NMR (75.5 MHz, −100 °C): δ 102.3 (C_8H_8), 29.7 (broad, PCH), 22.2 (PCH$_2$), 19.8, 18.0 (diastereotopic CH$_3$), d^{i}ppe. ^{31}P NMR (121 MHz, −100 °C): δ 78.7, ^1J(PtP) = 3271 Hz.

Isomer 6b. ^{1}H NMR (300 MHz, −100 °C): δ 6.53 (2H, HC5/HC8), 5.53 (2H, HC6/HC7), 5.13 (2H, HC2/HC3), 3.65 (2H, HC1/HC4), 1,4-η^2-C_8H_8; 2.47, 2.26 (each 2H, PCH and PC′H), 1.64 (4H, PCH$_a$H$_b$), 1.20, 1.12, 1.05, 0.98 (each 6H, two pairs of diastereotopic CH$_3$), d^{i}ppe. ^{13}C NMR (75.5 MHz, −100 °C): δ 149.1 (2C, C5/C8), 133.4 (2C, C2/C3), 123.3 (2C, C6/C7), 41.7 (2C, ^1J(PtC) = 456 Hz, C1/C4), 1,4-η^2-C_8H_8; ≈25 (4C obscured by solvent, PCH and PC′H), 23.2 (2C, PCH$_2$), 19.4, 19.0, 18.7, 18.1 (each 2C, two pairs of diastereotopic CH$_3$), d^{i}ppe. ^{31}P NMR (121 MHz, −100 °C): δ 67.2, ^1J(PtP) = 2238 Hz.

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