Normal and Anomalous Ring Opening of 1-3-η-Pentaarylcyclobutenylpalladium Complexes

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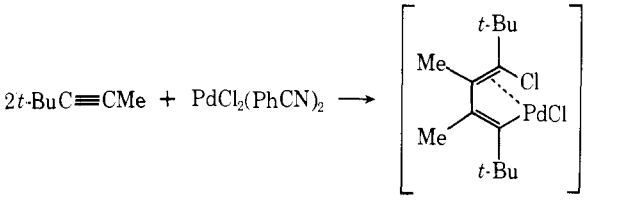
Abstract: Arylation (with $NaBPh_4$ in acetone) of the cyclobutadienepalladium complex, $[PdCl_2(C_4To_4)]_2$ (To = *p*-tolyl), gives the 1-3-η-cyclobutenyl complex $[Pd(C_4To_4Ph)Cl]_2$ with the phenyl group entering stereospecifically endo to the metal. Ring opening occurs on reaction of the monomeric $[Pd(C_4To_4Ph)X]$ (X = acac, S_2CNR_2) with ligands (in particular, $PPhMe_2$) to give the σ-butadienyl complexes $[Pd(C_4To_4Ph)X(PPhMe_2)]$, where the 1-3-$\eta$-cyclobutenyl ligand has opened stereospecifically in the expected conrotatory manner. In contrast, the cyclobutenyl dithiocarbamates $[Pd(C_4To_4Ph)(S_2CNR_2)]$ (**17**) undergo a spontaneous ring opening (2 days/20 °C or 2 h/60 °C) to give a mixture of the expected conrotatory ring-opened σ,π-butadienyl $[Pd(C_4To_4Ph)(S_2CNR_2)]$ [**20**, *p*-tolyls *E* on C(3), C(4)] and the unexpected, formally disrotatory, isomer [**21**, *p*-tolyls *Z* on C(3), C(4)] in a ca. 40:60 ratio, as shown by an x-ray structure determination, HPLC, and NMR spectroscopy. Investigations to elicit the route by which the isomer **21** is formed are described. The reaction **17** → **20** + **21** is unimolecular and does not appear to involve ionic intermediates or to be photochemically initiated. Free cyclobutenyl radicals are easily formed from these complexes and a convenient way is by reaction of cyclobutenyl complexes with $Ph_2PCH_2PPh_2$ (dppm); this also leads to the Pd(I) complex $[Pd_2Cl_2(dppm)_2]$. Evidence is presented *against* free radicals participating in the ring opening, and in favor of their being intermediates in decomposition side reactions. The reaction does not appear to proceed by a radical chain mechanism either. A mechanism is proposed which involves the conrotatory ring opening of **17** to give the expected isomer (**20**) which then equilibrates with the unexpected isomer (**21**) via a metallocyclopentenyl intermediate in which C(3) can flip from one side to the other.

Over the past few years considerable interest has developed in ring-opening and closing reactions in organometallic systems and the mechanisms by which they proceed. One of us has, in this context, shown that in the Pd(II)-induced oligomerization of disubstituted acetylenes bearing bulky substituents the chief products are cyclobutadiene complexes (e.g., **3**) which arise by a cyclization of intermediate σ-butadienyl complexes (e.g., **1**);[1,2] a presumed but so far unconfirmed further intermediate is a chlorocyclobutenyl complex (**2**).



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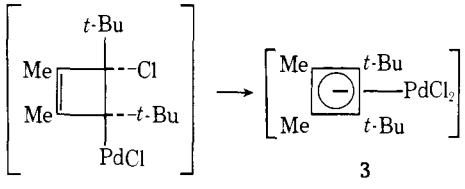

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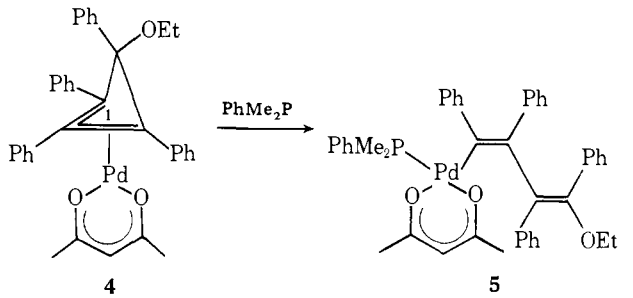
The opposite process, the opening of a cyclobutenyl complex, has been demonstrated by Powell et al. for the *endo*-alkoxytetraphenylcyclobutenylpalladium β-diketonate complex (**4**) to the σ-butadienyl complex (**5**).[3] This ring opening occurs stereospecifically and in the conrotatory mode expected for a concerted thermally allowed reaction.[4] Powell et al. also noted that the *exo*-alkoxy isomer of **4** did not undergo ring opening, which they ascribed to a possible "steric inhibition between phenyl groups in the transition state of a conrotatory ring opening" of the *exo*-alkoxy isomer.[3]



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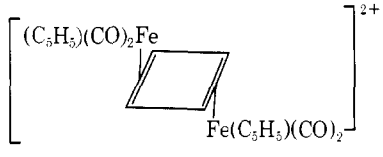
At least one other ring opening of a cyclic C_4 organometallic, **6** → **7**, has been described which can also be viewed as proceeding in a conrotatory manner.[5]



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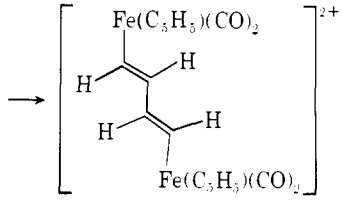

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Four different modes (a–d) of ring opening for an η^3-cyclobutenyl–metal complex may be envisaged, if the reasonable assumption is made that this proceeds via an η^1- (σ-) cyclobutenyl complex.

The reaction **4** → **5** is an example of the conrotatory mode (a) and **6** → **7** of the conrotatory mode (b); the disrotatory modes (c) and (d) have not so far been found.

To test whether the ring openings of C_4 organometallics invariably proceed in a conrotatory manner the reactions of cyclobutenylpalladium complexes as a function of coligand and charge have been examined.

In order to avoid complicating side reactions that would be possible if the substituents R^1 to R^5 in **8** contained >CH– groups (such as β-elimination of Pd–H) or were alkoxy or halo groups, and bearing in mind the limitations imposed by the need for convenient synthetic procedures for the compounds

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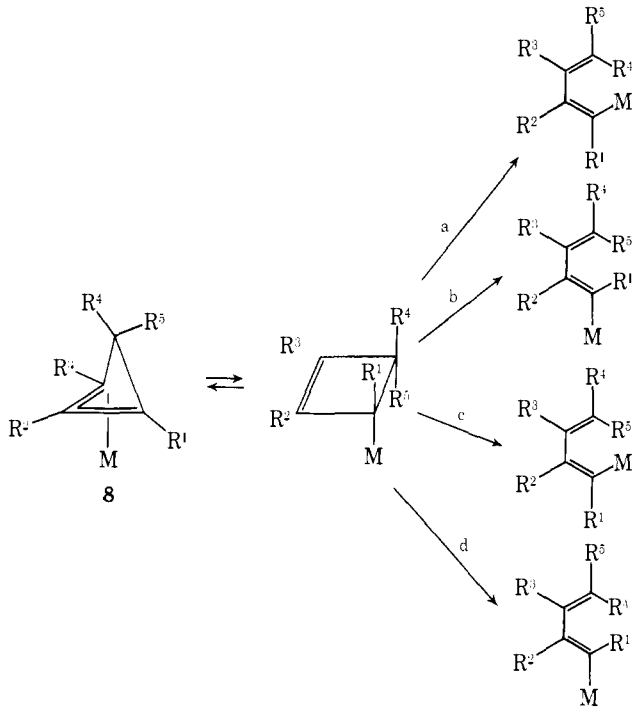

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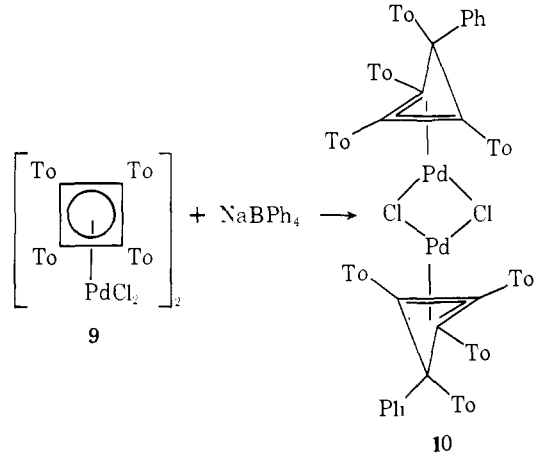
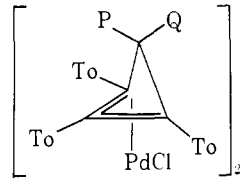
to be investigated, we focused on the reactions of pentaarylcyclobutenylpalladium complexes.

Results and Discussion

Cyclobutenylpalladium Complexes [Pd(C$_4$To$_4$Ph)XY]. The complex **10** was easily synthesized from the tetrakis-*p*-tolylcyclobutadienepalladium complex (**9**)[6] by reaction with sodium tetraphenylborate in acetone. Only one isomer was



9 **10**



11, P = *p*-tolyl; Q = OMe
12, P = OMe; Q = *p*-tolyl

formed which we expected to be the *endo*-4-phenyl-*exo*-4-*p*-tolyl (**10**) since we had previously established that $NaBPh_4$ reacts with [Pd(diene)Cl$_2$] complexes to effect endo phenylation of the organic ligand.[7] That **10** was indeed the anticipated isomer was shown by a comparison of its 220-MHz ^{1}H NMR spectrum with those of the *endo*- and *exo*-methoxytetrakis-*p*-tolycyclobutenylpalladium complexes **11** and **12** the structures of which are securely based.[1,8] The close similarity between the spectra of **10** and **11** in the aromatic region and

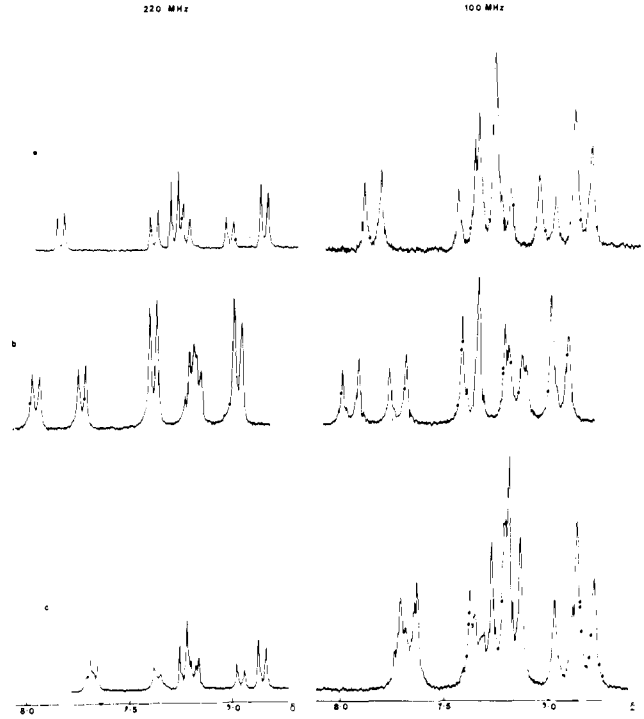


Figure 1. The 100-MHz and the 220-MHz ^{1}H NMR spectra of top, the *endo*-methoxycyclobutenyl complex (**11**), middle, the *exo*-methoxycyclobutenyl complex (**12**), and bottom, complex **10**, in the aromatic region.

the difference between either of these and that of **12** (Figure 1) allows an unambiguous assignment to be made.

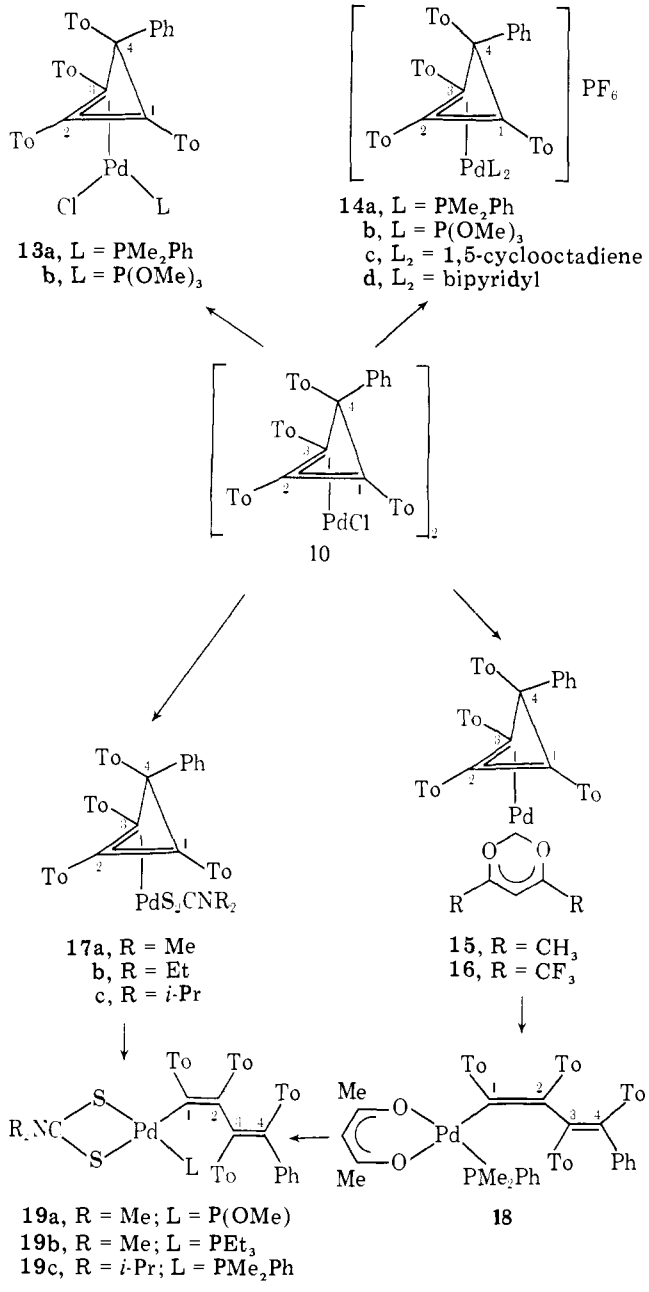
Reaction of the chloride bridged dimer **10** with *tert*-phosphine or phosphite ligands gave the monomeric complexes **13a** or **13b.** Other monomeric complexes were the β-diketonates **15** and **16** obtained from reaction of **10** with Tl(RCOCHCOR) (R = CH_3 and CF_3, respectively) and the dithiocarbamates **17a–c** from **10** and NaS_2CNR_2 (R = Me, Et, and *i*-Pr, respectively).

A further series of complexes were the cations $[Pd(C_4To_4Ph)L_2]^+$; when the chloro complex **10** was reacted with $AgPF_6$ in acetone–dichloromethane, AgCl was precipitated and a yellow solution, presumably containing **14** (L = acetone), was obtained. Addition of 2 equiv of PMe_2Ph or $P(OMe)_3$ gave **14a** or **14b;** the analogous compounds **14c** and **14d** were prepared by adding 1,5-cyclooctadiene (cod) and bipyridyl (bpy), respectively, to the acetone solvent species in situ (Scheme I).

All of these compounds were fully characterized by analysis and NMR spectroscopy (Tables I–III). While the ^{1}H spectra were extremely complex, resolution of the *p*-tolyl methyl signals into three singlets (intensity ratio 2:1:1) occurred for complexes **10, 14c, 15, 16,** and **17a–c.** This is the result anticipated for the structures shown for these molecules as in each case they possess a plane of symmetry through C(2), C(4), and Pd. By contrast, the complexes **13a** and **13b,** which have no such plane of symmetry, showed four equal intensity singlets arising from four inequivalent *p*-tolyl methyl substituents. The expected 2:1:1 splitting of these peaks was not observed (even at 220 MHz) for the cationic complexes **14a, 14b,** and **14d,** which exhibited only two resonances in a 1:3 intensity ratio, presumably due to accidental equivalence.

The ^{13}C NMR spectra were very helpful in assigning the cyclobutenyl structures, largely owing to the C_4 ring resonances C(1), C(3), and C(4), which came in areas of the spectrum free of other resonances. Although the precise positions of these resonances varied somewhat, we may assign with confidence the range δ 66–71 to C(4) and the range δ 83–113, depending

Scheme I



on charge and coligands to C(1) and C(3). In the neutral complexes C(2) was generally observed toward the lower field end of the range, δ 119–126. Resonances in the cod and bpy complexes **14c** and **14d** at δ 125.0 and 126.7 may also be assigned to C(2), but in **14a** and **14b**, and probably in **13a** and **13b**, these resonances have moved into the region rich with aromatic carbons and only tentative assignments are possible. These ranges are in agreement with assignments in related molecules.[9-12]

In the cationic PX_3 complexes **14a** and **14b** the resonances due to C(4) are triplets [J(C–P) = 7–8 Hz] due to coupling to two equivalent ^{31}P nuclei. However, the triplets seen for C(1) [≡ C(3)] arise from "virtual" coupling of these carbons to both (now inequivalent) ^{31}P nuclei and the splitting parameter is best defined by $N(C-P)^9 = [|J(C-P^1) + J(C-P^2)|]$, which is 36 for **14a** and 62 Hz for **14b**. In the mono-PX_3 complexes **13a** and **13b** C(4) is unambiguously assignable as the doublet at δ ca. 68 [J(C–P) = 5 or 8 Hz], and we propose that the doublets at δ 113.1 (**13a**) [J(C–P) = 29 Hz] and 111.3 (**13b**) [J(C–P) = 46 Hz] be assigned to C(1) trans to PX_3 while those at δ 85.5 (J = 9 Hz) (**13a**) and 87.2 (J = 14 Hz) (**13b**) be assigned to C(3) cis to PX_3.

Since these have not previously been reported, the ^{13}C NMR spectra of three *endo*- or *exo*-methoxytetrakis-*p*-tolylcyclobutenyl complexes are also included in Table I; it will be seen that they are consistent with the other cyclobutenyl complexes reported except that C(4) comes at lower field (δ 88–91).

Conrotatory Cyclobutenyl Ring-Opening Reactions. The pentanedionato compound **15** underwent reaction with dimethylphenylphosphine to give the adduct **18** in which ring opening had occurred. This was immediately evident from the NMR spectra; in particular the ^{13}C spectrum showed the absence of the higher field peaks assigned to the cyclobutenyl ring carbons, C(1)–C(4). Instead, a new doublet was observed at very low field [δ 152.9, J(C–P) = 5 Hz] which we assign to C(1) of the σ-butadienyl ligand in **18**, coupled to a *cis*-Me_2PhP ligand; C(2)–C(4) are not assignable as they cannot be separated from the aromatic non-proton-bearing carbons.

Further evidence for ring opening was shown by the pentanedionato ligand which no longer had a plane of symmetry as in **15**, two resonances being observed for both the carbonyl and methyl carbons. The proton spectra were, as usual, complex, but all the *p*-tolyl methyls were now distinguishable as separate resonances, which had also moved upfield by comparison with those of complex **15**.

The NMR spectra were not helpful in assigning stereochemistry to the σ-butadienyl ligand, and an x-ray structure determination was carried out.[13] This indicated the ligand to have the geometry depicted and showed that the cyclobutenyl ring in **15** had opened in a conrotatory manner identical with **4** → **5**, mode (a). This finding disproves the suggestion[3] that steric inhibition between two phenyls may be the cause of the absence of ring opening in the *exo*-alkoxy complex (**12**, phenyl in place of *p*-tolyl).

It was also shown by a series of NMR experiments that **15** underwent ring opening on reaction with $P(OMe)_3$, PEt_3, *t*-BuNC, and SMe_2. In each case the ^1H spectra showed the inequivalence of the acac methyls and the shift to higher field of the *p*-tolyl methyls characteristic of the ring-opened adducts. Only one ring-opened isomer was produced in each reaction as was clear from the NMR spectra.

By contrast, the hexafluoropentanedionato complex **16** did not ring open when treated with $PPhMe_2$. Attempts were also made to ring open the cationic complexes **14a–d** but these again failed. Reaction of the cod complex **14c** with dimethylphenylphosphine gave **14a** and there was no detectable reaction of **14a** with lithium chloride. No complexes could be isolated on reaction of **14a** with excess PMe_2Ph or on reaction of **14b** with $P(OMe)_3$ and only decomposition with liberation of an organic ligand could be detected. *It appears, therefore, that such ring-opening reactions are inhibited in positvely charged complexes and also by electron-withdrawing ligands on the metal.*

Anomalous Ring Opening of Cyclobutenyl Complexes. Ring-opening reactions of the dithiocarbamates **17a–c** were also examined. Most work was concentrated on the last of these complexes, **17c**, since it was the most soluble and hence the easiest to study by NMR spectroscopy, particularly at low temperatures. All the properties of the complexes **17a–c** were in agreement with the structures proposed.

The following reactions of **17** with ligands were shown by NMR spectroscopy to give ring-opened products: **17a** + $P(OMe)_3$, PEt_3, *t*-BuNC, or SMe_2, and **17c** + PMe_2Ph. The complexes **19a–c** were isolated and characterized. Again, the ^{13}C NMR spectra of **19a** and **19c** (**19b** was insufficiently soluble) showed the absence of the characteristic resonances of the cyclobutenyl carbons C(1)–C(4), but did show the very low field doublet due to C(1) in the σ-butadienyl ligand.

In each case only one ring-opened isomer could be detected.

Proof that ring opening had occurred in the same conrotatory manner as for **15** → **18** was obtained by reaction of complex **18** with NaS_2CN-*i*-Pr_2; this gave a single isomer identical with **19c.**

It was then discovered that the dithiocarbamates **17** also underwent facile isomerization reactions even in the absence of added ligand. Evidence was accumulated for the occurrence of a similar process for the pentanedionato compound **15** but this reaction was not clean and proceeded only slowly with substantial by-product formation. When the dimethyldithiocarbamate complex **17a** was refluxed in chloroform for 2 h in the absence of added ligand, a rather poorly soluble new complex (A) was obtained. This was monomeric in solution and the S_2CNMe_2 methyls were no longer equivalent, either in the ^{13}C or the ^1H NMR spectra. Further, a resonance at δ 147.4 (in the ^{13}C spectrum) suggested the presence of a σ-butadienyl ligand, and two other resonances, at δ 103.4 and 123.0, can be assigned to π-bonded olefinic carbons. The ^{13}C spectrum also showed that some of the peaks were doubled or broadened and suggested the presence of isomers. This was supported by the observation that reaction of A with HCl gas gave the organic diene, CHTo=CToCTo=CPhTo, as two isomers (each with a parent ion *m/e* 490, as expected), which were only resolvable by HPLC.

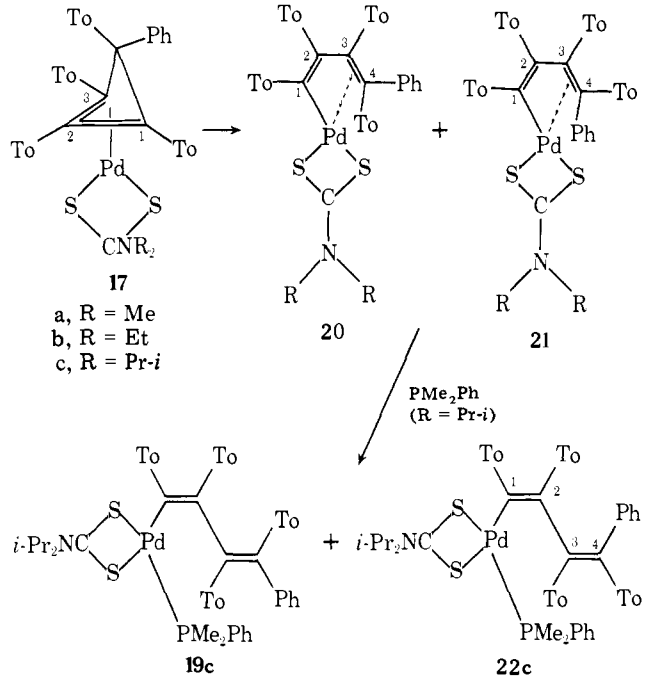
To investigate this problem further the reactions of the more soluble diisopropyl derivative **17c** were investigated. Again, on refluxing in chloroform for 2 h (or as we subsequently found, in solution at 20 °C for 2 days) a rearrangement occurred to give a new material (C) which was also monomeric. When C was reacted with dimethylphenylphosphine a mixture of two isomers was obtained as shown, for example, by the ^1H NMR spectrum which showed seven peaks due to the *p*-tolyl methyls (in the ratio of 1:1:1:2:1:1:1), four of which were coincident with those of the single isomer **19c.** Confirmation of this came from HPLC studies on these compounds; the mixture gave two peaks in the ratio of ca. 45:55, and the single material **19c** only showed one, which was coincident with one of the peaks in the mixture.

The ^{13}C NMR spectrum of the mixture (C) was complicated by the existence of a dynamic process associated with restricted rotation of the isopropyl groups about the N-*i*-Pr bonds. Thus, at 60 °C two resonances may be assigned to C(1) (δ 149.9, 150.1) and also to C(4) (δ 107.5, 108.5) but on cooling these broaden (at room temperature) and finally sharpen to reveal four resonances at low temperatures: C(1) (CD_2Cl_2/−70 °C) at δ 147.4, 149.3, 149.7, and 149.9 and C(4) ($CDCl_3$/−60 °C) at δ 102.0, 102.3, 102.8, and 103.2.

In order to define the nature of the mixture (C) an x-ray crystal structure determination was undertaken of a single crystal. The results are explained in detail in the accompanying paper,[13] but from the standpoint of the work described here the exciting result was the discovery that the crystal contained molecules of two isomers arranged in precisely the same manner. Both isomers contained the identical dithiocarbamate and a σ,π- (or 1:3,4-η-) butadienyl ligand and the only difference between them was the relative orientations of the phenyl and *p*-tolyl substituents at C(4). This manifested itself as a disorder of one methyl attached to the phenyls at C(4). In the major isomer (**21c,** 60 ± 2%) the tolyls at C(3) and C(4) were cis (*Z*) and in the minor component (**20c,** 40 ± 2%) they were trans (*E*).

The second isomer arising from reaction of mixture C with dimethylphenylphosphine must therefore have structure **22c.**

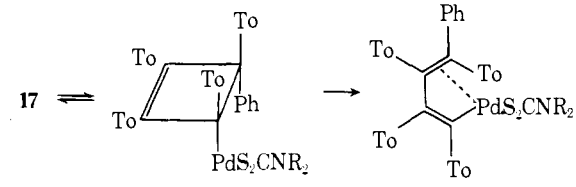
The crystal structure of complex C (**20c** and **21c**) showed a planar arrangement of the atoms S_2CNC_2, implying substantial double-bond character in the S_2C–N bond. The isopropyl groups were fixed as shown[13] and there was no significant disordering. It is likely, however, that in solution there is



slow rotation about the N-*i*-Pr bonds leading to complete equilibration.[14]

Similar results were also obtained on heating a sample of the diethyldithiocarbamate complex (**17b**); this produced a mixture (B) analogous to A and C. However, in contrast to C only two species (corresponding to **20b** and **21b**) were present either at −70 or at 40 °C, as would be expected since the barrier to rotation about the N–Et bonds should be much less than that about N-*i*-Pr bonds.

Mechanism of the Anomalous Ring Opening. Following the arguments developed above, the rearrangements **17** → **20** are examples of conrotatory ring openings. However, by this reasoning **21** arises from the σ-cyclobutenyl intermediate **24** by a mechanism which, if concerted, is disrotatory and should only be photochemically allowed.



In order to examine this reaction further a number of tests were applied to ascertain if evidence could be obtained against a concerted unimolecular process and hence in favor of a stepwise mechanism which would not violate the principles established for organic reactions. There has, over the years, been lively and sustained discussion on whether metals with accessible d orbitals have the ability to lift these symmetry-based constraints. The current general concensus is that metals have no such detectable property and in cases where they appear to induce reactions that violate these principles close examination has always shown that a series of simple and allowed stepwise processes is occurring.[19]

That the reaction **17c** → C is unimolecular was shown by the lack of change of rate when the concentration in $CDCl_3$ was altered by a factor of 5. There was also no change in rate when it was carried out in benzene (dielectric constant, ε, 2.28) or in nitrobenzene (ε 35.7); this suggests that no ionic or highly polar intermediates are involved in the rate-determining step.

Reactions carried out in the dark were compared to those

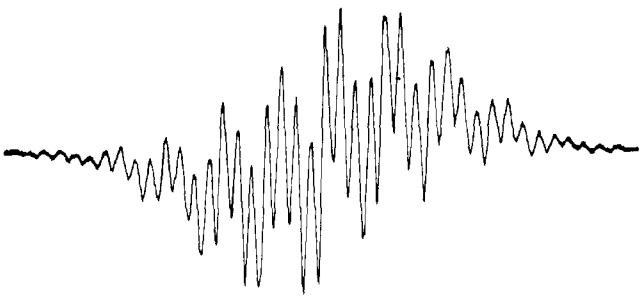
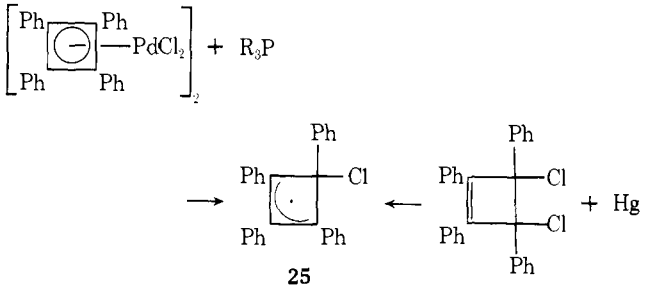


Figure 2. The ESR spectrum of C_4To_4Ph (**26**).

run in the presence of light, and again no detectable differences in rate could be observed. Furthermore, irradiation (366 nm) of a dichloromethane solution of **17c** at −78 °C caused no isomerization to ring-opened compounds; this reaction would have been expected to produce only isomer **21c** if it were a photochemically induced process. We conclude therefore that no photochemical processes are occurring during the ring opening. Further experiments also indicated that there was no change in isomer ratios when the ring-opened mixture (C) was irradiated; however, some decomposition did occur. This suggests either that C is the equilibrium mixture or that no photochemical isomerization about the C(3)–C(4) bond is occurring.

Work, chiefly by Sandel and Freedman,[20] has shown that 4-halotetraphenylcyclobutenyl radicals (**25**) can easily be generated from organometallic precursors and that such radicals have long lifetimes.[21,22]



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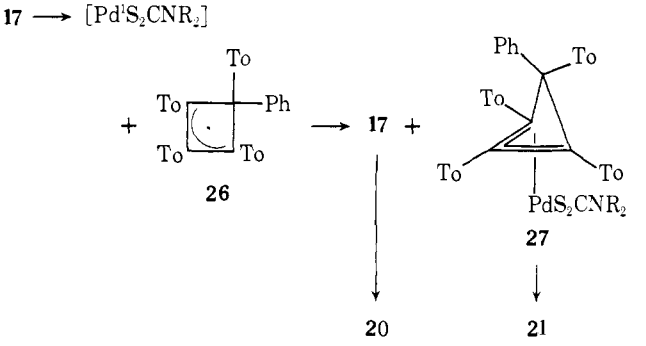
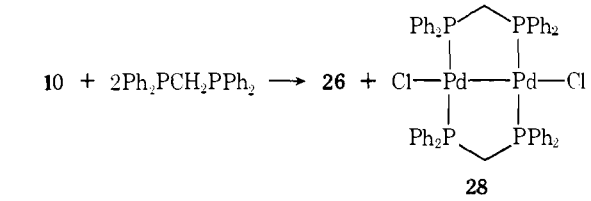
A further possible mechanism for the reaction of **17c** → C could therefore be by homolytic cleavage of the σ-cyclobutenyl complex **24** to generate **26** which can then recombine with the Pd^I-dithiocarbamate fragment either to the same face of the cyclobutene that was originally bound to the metal or to the other side, to give isomeric cyclobutenyl complexes **17** + **27** which then both open normally in a conrotatory manner to give the observed mixture (C).



26 **20** **21** **27**

In order to test the feasibility of a radical mechanism, the complex **10** was reacted with the chelating diphosphine 1,2-bis(diphenylphosphino)methane (dppm), which has a high tendency to stabilize metal–metal bonded species in unusual oxidation states,[23] and would thus assist the formation of a Pd(I) species and hence the radical **26.**

Addition of dppm to a degassed solution of the chlorine-bridged dimer **10** gave a dark green solution which was stable under nitrogen for about 24 h at 20 °C. The solution showed a strong ESR spectrum (and indeed the appearance of a strong green color appears to be characteristic of arylcyclobutenyl radicals[20,22]) and from the solution a 68% yield of the expected Pd(I) complex **28** was isolated.



28

The ESR spectrum (Figure 2) consisted of an odd number of principal lines, at least 9 and probably 11, each split into a quintet, with coupling constants 3.5 and 0.88 G, respectively, and was clearly due to only a single species.[24,25] The complexity of the system and the impossibility of unambiguously establishing the very weak outermost lines of the spectrum prevented a complete analysis. However, in **25** the electron was found to couple primarily to the six ortho and para hydrogens of the 1- and 3-phenyls of the cyclobutenyl ring with $a_{ortho} \approx a_{para} =$ 2.94 G and secondarily to the four meta hydrogens of the same phenyls with $a_{meta} = 0.94$ G. The spectrum observed in this work can be assigned to **26** if coupling again only occurs to the aryl groups 1 and 3 and if $a_{ortho} \approx a_{CH_3} = 3.5$ G[26] (i.e., a total of 10 protons), further coupled to four meta hydrogens, a_{meta} = 0.88 G. This would require an 11 by 5 line spectrum, consistent with our results.

The same ESR spectrum together with the characteristic green color was observed in a variety of other reactions, including that of $PPhMe_2$ with **17c** and with **14a;** the ESR spectrum was also seen, weakly at 80 °C, more strongly (associated with a deep red color) at 105 °C, when a toluene solution of **17c** was heated and also when a solution of C was heated.

Clearly then, cyclobutenyl radicals are easily accessible from most of these complexes; however, the detection of free radicals does not prove that they are involved in the ring-opening reactions. Indeed the data we have indicate that the radical forming paths are *not* associated with the ring opening but rather with independent decomposition side reactions. Evidence in favor of this is as follows.

(1) *No* radicals are detected in the 20 °C isomerization of **17c** to C and the yield at 20 °C (73%) is significantly higher than that at 60 °C (62%).

(2) Radicals *are* detected in the 20 °C reaction of **17c** to **19c,** which, however, produces only the "normal" isomer. Furthermore, although NMR spectroscopic monitoring shows the reaction to be complete after a very few minutes, the radicals persist much longer.

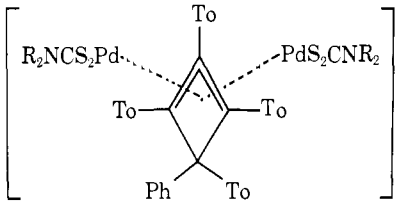
(3) No isomerization of an *endo*-phenyl-*exo*-tolyl to an *endo*-tolyl-*exo*-phenyl η^3-cyclobutenyl isomer has been detected, even in cases such as **14a** + $PPhMe_2$, where radicals are produced.

CIDNP experiments gave wholly negative results; when the isomerization **17c** → C was carried out in nitrobenzene at 100 °C and the NMR spectrum monitored every 10 s, *no* significant signal enhancements or negative peaks could be observed. Furthermore, when a solution of **17c** was mixed with one of $PPhMe_2$ at −196 °C and allowed to warm to −78 ° a color change to red occurred. The reaction was monitored every 2.1 s by NMR spectroscopy at −10 °C (to achieve a reasonable rate for the formation of **19c**); no CIDNP effects and no green coloration were observed even though the same product, **19c,** was formed as at 20 °C.

We conclude therefore that free cyclobutenyl radicals, such

as **26**, although easily produced in the reactions under consideration, probably play no significant role in the ring opening and indeed arise from decomposition side reactions.

One other possible mechanism involves a radical chain reaction. If a small amount of decomposition occurred in the sense **17** → $[PdS_2CNR_2]$ + **26**, this would generate a Pd^I species which might be able to attack a further molecule of **17** at the other face of the cyclobutenyl ring giving **27** via a transition state Y.



Y

When 10 mol % of tetramethylthiuram disulfide $[Me_2NC(S)S{\cdot}SC(S)NMe_2]$ was added to a solution of **17c**, there was no change in the rate of isomerization to C and, apart from a small amount of exchange of i-Pr_2NCS_2 for Me_2NCS_2, the reaction proceeded identically with the normal isomerizations. Since the thiuram disulfide would certainly scavenge any $Pd^IS_2CNR_2$ produced this experiment eliminates a radical chain process as well.

If radical and photochemical processes are thus excluded as explanations for the reaction **17c** → C and if the rules governing the ring opening are the same for organometallic as well as for purely organic reactions then an alternative explanation must hold. The most probable such process involves a ring opening in the normal conrotatory sense **17** → **20**, followed by a stereomutation which allows equilibration of the butadienyl ligand **20** ⇄ **21** to occur. Such reactions are not uncommon in organic systems but they usually involve photochemical, radical, acid, or base catalysis,[27] which may be excluded here.

For the reaction **20** → **21** reorganizations involving a 180° twist about the coordinated C(3)–C(4) bond are unlikely for both steric and electronic reasons. It is in principle possible for the required stereomutation to take place if C(3)–C(4) is first decomplexed from the metal and then a twist is allowed to occur about this bond followed by a recomplexation, but such a process should involve a solvated three-coordinated Pd intermediate and should therefore be solvent dependent.

A much simpler explanation which is in agreement with all our data is illustrated in Figure 3 and merely involves a conformational flip in a metallocyclopentenyl ring. The crystal structure of **20c** and **21c** shows the metal to be fractionally closer to C(4) [2.278 (9) Å] than to C(3) [2.302 (9) Å] and only about 0.2 Å further away from C(4) than would be expected for a Pd–C σ bond. The formation of a metallocyclopentenyl intermediate (iii) from the ground state (i) is therefore likely to require only a small amount of reorganization. Models of iii show that the metallocyclopentenyl ring is close to planar[28] and C(3) and its substituent can then either move back again giving ii and hence i, or it can move in the opposite sense giving iv and hence v. The overall process corresponds to the equilibration **20** ⇆ **21** and may be expected to be a moderately low energy path for the stereomutation.[29] The relative amounts of **20c** and **21c** present in the mixture C are therefore the thermodynamically expected ratios.

Although the complexity of the NMR spectra of C made determination of the relative amounts of **20c** and **21c** very difficult, it did appear that the lower temperature isomerization of **17c** gave more of one isomer (presumably **20c**) than the 60 °C isomerization. When the lower temperature mixture was heated a change in the NMR spectrum was observed which was consistent with the attainment of the equilibrium ratio.

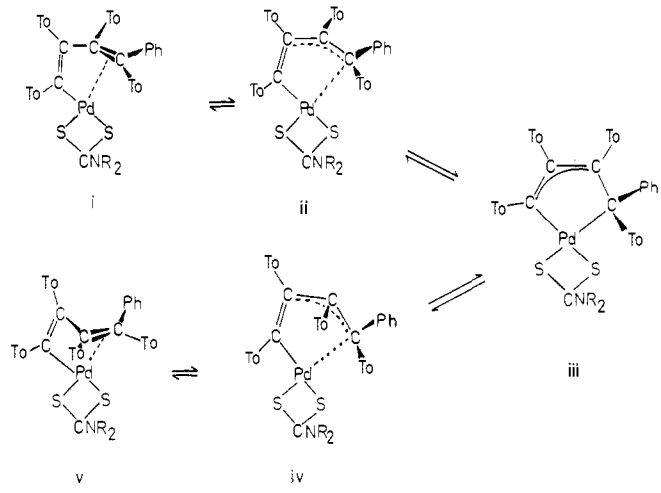


Figure 3. Proposed path for stereomutation of **20** and **21** via a metallocycle flip.

Such a stereomutation via metallocycle flip would only be expected to occur if the double bond C(3)–C(4) is coordinated and is therefore lengthened and hence has a lower bond order than a normal carbon–carbon double bond. In support of this point it is relevant that all attempts to isomerize the dimethylphenylphosphine adduct (**19c**), which has an uncoordinated σ-butadienyl ligand, to the equilibrium mixture **22c** + **19c** (obtained from C) failed.

Two related processes, the cis–trans isomerization of the methyl in η^4-coordinated piperylene in $[Mo(C_5H_5)(CO)_2(CH_2{:}CHCH{:}CHMe)]^+$ [30] and a Rh(I)-catalyzed cis–trans isomerization accompanied by an epimerization in 7-(β-deuteriovinyl)bicyclo[4.1.0]heptane[31] have recently been interpreted in an analogous way. It is likely that reactions of this type are quite common and that many more will be uncovered.

Experimental Section

Unless otherwise stated all reactions were carried out in an atmosphere of nitrogen. NMR data are collected in Tables I and II and microanalytical data and decomposition points in Table III.

[Pd(1-3-η-C_4To_4Ph)Cl]$_2$ (10). $NaBPh_4$ (2 g, 5.7 mmol) was added slowly to a stirred solution of $[PdCl_2(C_4To_4)]_2$[6] (**9**, 2 g, 1.7 mmol) in acetone (300 mL) at 0 °C. After 1.5 h the brown solution was reduced to low volume in vacuo, flushed with nitrogen again, and left to stand at 0 °C for 18 h. The crude yellow product was filtered off and washed with acetone. Chromatography in CH_2Cl_2 on silica gel followed by crystallization from CH_2Cl_2/MeOH at 0 °C gave the product as orange crystals, yield 1.4 g (63%).

[Pd(1-3-η-C_4To_4OMe)Cl]$_2$ (11). A solution of $PdCl_2$ (500 mg, 2.8 mmol) and NaCl (330 mg, 5.6 mmol) in hot water (5 mL) was filtered into a stirred suspension of di-*p*-tolylacetylene (1.2 g, 5.3 mmol) in methanol (50 mL). After standing at 20 °C for 24 h, the product was collected by filtration and crystallized from CH_2Cl_2/hexane to give mustard-yellow crystals, yield 1.3 g (79%).

[Pd(1-3-η-C_4To_4OMe)Cl]$_2$ (12). $[PdCl_2(C_4To_4)]_2$[6] (2 g, 1.7 mmol) was stirred overnight in suspension in MeOH (40 mL) containing Na_2CO_3 (180 mg, 1.7 mmol). The mustard-colored precipitate was collected and purified by filtering through a short silica gel column in CH_2Cl_2. Crystallization from CH_2Cl_2/MeOH gave **12** as orange crystals, yield 1.8 g (90%).

[Pd(1-3-η-C_4To_4Ph)Cl(PMe_2Ph)] (13a). PMe_2Ph (170 μL, 1.0 mmol) was added dropwise to a stirred solution of **10** (500 mg, 0.4 mmol) in CH_2Cl_2 (20 mL). After removal of solvent the remaining orange oil was chromatographed in ether on silica gel, the first orange fraction being collected. Crystallization first from ether/hexane and then from CH_2Cl_2/MeOH at 0 °C gave **13a** as brick-red crystals, yield 0.37 g (60%). The complex [Pd(1-3-η-C_4To_4Ph){$P(OMe)_3$}Cl] (**13b**) was obtained in a similar way in 74% yield.

[Pd(1-3-η-C_4To_4Ph)(1,5-cod)]PF_6 (14c). $AgPF_6$ (0.23 g, 0.9 mmol) was added to a stirred solution of complex **10** (0.50 g, 0.4 mmol) in

Table I. ^{13}C {^1H} NMR Spectra (Chemical Shifts in ppm, Coupling Constants in Hz)

Compd	C(1)	C(2)	C(3)	C(4)	Aromatics	*p*-Tolyl methyl	Other
[Pd(1-3-η-C_4To$_4$Ph)Cl]$_2$[a] (**10**)	89.6	119.4	89.6	70.3	141.9, 140.7, 138.6, 137.4, 135.8, 130.4, 129.8, 129.2, 128.9, 128.1, 127.1	21.5, 20.8	
[Pd(1-3-η-C_4To$_4$OMe)Cl]$_2$[a] (endo-OMe) (**11**)	89.7	115.9	89.7	90.8	139.1, 138.3, 137.7, 136.6, 130.1, 129.1, 128.1, 126.5	21.5, 20.9	55.9 O*C*H$_3$
[Pd(1-3-η-C_4To$_4$OMe)Cl]$_2$[a] (exo-OMe) (**12**)	89.8	119.2	89.8	89.2	139.2, 138.2, 137.4, 129.7, 129.3, 128.8, 128.1, 127.9	21.6	51.7 O*C*H$_3$
[Pd(1-3-η-C_4To$_4$Ph)·(PMe$_2$Ph)Cl][b] (**13a**)	113.1 d J[C–P] = 29	*c*	85.5 d J[C–P] = 9	68.4 d J[C–P] = 5	141.7, 139.1, 138.3, 137.2, 136.5, 135.4, 134.0, 132.8, 131.3, 130.8, 130.4, 130.2, 129.7, 129.4, 129.2, 128.9, 128.6, 128.4, 128.3, 127.9, 127.7	21.5, 20.9	14.1 d J[C–P] = 24 11.5 d J[C–P] = 24 P(*C*H$_3$)$_2$Ph
[Pd(1-3-η-C_4To$_4$Ph)-{P(OMe)$_3$}Cl][b] (**13b**)	111.3 d J[C–P] = 46	*c*	87.2 d J[C–P] = 14	68.1 d J[C–P] = 8	141.8, 139.8, 138.5, 137.9, 137.6, 136.7, 131.9, 131.5, 130.7, 130.0, 129.6, 129.4, 129.0, 128.4, 127.8	21.5, 20.9	51.7 P(O*C*H$_3$)$_3$
[Pd(1-3-η-C_4To$_4$Ph)-(PMe$_2$Ph)$_2$]PF$_6$[a] (**14a**)	107.1 t N[C–P] = 36	134.2 t J[C–P] = 18	107.1 t N[C–P] = 36	66.9 t J[C–P] = 7	140.1, 139.4, 139.2, 136.8, 135.3, 131.8, 131.6, 130.4, 130.2, 123.0, 129.7, 129.0, 128.9, 127.9, 126.8	21.5, 20.9	13.0 m, 12.2 m P(*C*H$_3$)$_2$Ph
[Pd(1-3-η-C_4To$_4$Ph)-{P(OMe)$_3$}$_2$]PF$_6$[a] (**14b**)	107.1 t N[C–P] = 62	134.1 t J[C–P] = 13	107.1 t N[C–P] = 62	66.6 t J[C–P] = 8	140.5, 138.9, 136.8, 133.0, 129.9, 129.4, 129.0, 128.7, 126.6	21.4, 20.9	52.5 P(O*C*H$_3$)$_3$
[Pd(1-3-η-C_4To$_4$Ph)-(COD)]PF$_6$[a] (**14c**)	109.8	125.0	109.8	66.9	141.5, 140.9, 139.7, 137.7, 132.6, 131.7, 130.2, 130.0, 129.2, 128.8, 127.8, 126.2		
[Pd(1-3-η-C_4To$_4$Ph)-(bpy)]PF$_6$[a] (**14d**)	92.1	126.7	92.1	69.5	140.9, 140.0, 139.7, 139.5, 136.8, 130.3, 129.9, 129.8, 129.4, 128.6, 128.3, 127.5, 127.2, 127.0	21.6, 21.4, 20.9	153.4, 148.6 bipy
[Pd(1-3-η-C_4To$_4$Ph)-(acac)][b] (**15**)	83.5	121.3	83.5	71.0	142.9, 142.6, 139.7, 137.8, 136.0, 131.8, 129.7, 129.3, 129.1, 128.4, 127.2	21.5, 21.0	188.1 (CH$_3$*C*O)$_2$CH; 99.6 (CH$_3$CO)$_2$*C*H; 28.3 (*C*H$_3$CO)$_2$CH
[Pd(1-3-η-C_4To$_4$Ph)-(hfacac)][b] (**16**)	88.5	122.4	88.5	71.4	141.8, 141.4, 140.5, 139.1, 137.1, 130.6, 129.9, 129.5, 129.0, 128.6, 128.4, 128.1, 127.7, 127.5	21.5, 20.9	176.0 q J[C–F] = 34 (CF$_3$*C*O)$_2$CH; 118.2 q J[C–F] = 285 (*C*F$_3$CO)$_2$CH; 89.6 (CF$_3$CO)$_2$*C*H
[Pd(1-3-η-C_4To$_4$Ph)-(S$_2$CNMe$_2$)][b] (**17a**)	90.8	125.5	90.8	69.8	143.1, 141.3, 139.4, 137.2, 136.3, 133.0, 129.5, 129.1, 128.0, 127.1	21.4, 21.5, 21.0	211.0 S$_2$*C*N(CH$_3$)$_2$; 40.7 S$_2$CN(*C*H$_3$)$_2$
[Pd(1-3-η-C_4To$_4$Ph)-(S$_2$CN-*i*-Pr$_2$)][b] (17c)	90.5	125.7	90.5	69.8	143.3, 141.4, 139.2, 136.9, 136.1, 133.2, 129.4, 129.2, 128.0, 127.8, 126.9	21.3, 21.5, 20.9	209.6 S$_2$*C*N{CH(CH$_3$)$_2$}$_2$; 51.7 S$_2$CN{*C*H(CH$_3$)$_2$}$_2$; 19.9 S$_2$CN{CH(*C*H$_3$)$_2$}$_2$
[Pd(η^1-C_4To$_4$Ph)-(acac)PMe$_2$Ph)][b] (**18**)	152.9 d J[C–P] = 5	*c*	*c*	*c*	146.0, 145.7, 145.2, 144.4, 143.4, 142.1, 141.2, 140.8, 136.4, 135.2, 135.0, 134.5,	21.2, 21.1	186.9, 186.6 (CH$_3$*C*O)$_2$CH; 99.4 (CH$_3$CO)$_2$*C*H); 28.0, 27.7 (*C*H$_3$CO)$_2$CH; 11.2 d

					133.2, 132.7, 132.3, 131.5, 130.9, 130.3, 129.9, 129.7, 129.0, 128.1, 127.7, 127.5, 127.4, 127.2, 126.6, 125.2		J[C–P] = 31, 9.8 d J[C–P] = 36 $P(CH_3)_2Ph$
[Pd(η^1-C_4To_4Ph)-(S_2CNMe_2)$P(OMe)_3$] (19a)	160.1 d J[C P] = 5	*c*	*c*	*c*	147.9, 147.6, 146.3, 142.8 142.6, 142.1, 141.7, 139.8, 135.1, 134.9, 133.2, 132.6, 132.5, 131.5, 130.6, 130.5, 127.9, 127.7, 127.4, 126.7, 125.3	21.4, 21.1, 20.9	211.0 S_2CNMe_2; 39.4 d J[C–P] = 3, 38.8 $S_2CN(CH_3)_2$; 51.7 $P(OCH_3)_3$
[Pd(η^1-C_4To_4Ph)-(S_2CNMe_2)PEt_3][e] (19b)							
[Pd(η^1-C_4To_4Ph)-(S_2CN-*i*-Pr_2)PMe_2Ph][a]	161.4 d J[C–P] = 6	*c*	*c*	*c*	146.9, 146.6, 146.3, 145.5, 143.8, 143.0, 141.8, 141.3, 139.3, 136.8, 135.2, 134.2, 132.9, 132.0, 131.1, 130.4, 130.1, 129.7, 128.9, 128.5, 127.7, 127.3, 126.8, 126.3, 124.6	21.2, 20.9	209.7 $S_2CN\{CH(CH_3)_2\}_2$; 50.7, 50.0 $S_2CN\{CH(CH_3)_2\}_2$; 20.2, 19.8 $S_2CN\{CH(CH_3)_2\}_2$; 13.3 d J[C–P] = 26, 10.6 d J[C–P] = 27 $P(CH_3)_2Ph$
[Pd(η^1-C_4To_4Ph)-(S_2CN-*i*-Pr_2)(PMe_2Ph)][a] (22c + 19c)	161.5 d	*c*	*c*	*c*	146.9, 146.7, 146.3, 146.2, 145.6, 145.0, 143.9, 143.1, 142.5, 141.9, 141.3, 139.4, 136.9, 135.2, 134.3, 132.9, 132.0, 131.1, 130.4, 129.8, 128.9, 128.5, 127.8, 127.3, 126.8, 126.5, 124.8	21.3, 21.0	209.7 $S_2CN\{CH(CH_3)_2\}_2$; 50.7, 50.1 $S_2CN\{CH(CH_3)_2\}_2$; 20.3, 19.9 $S_2CN\{CH(CH_3)_2\}_2$; 13.3 d J[C–P] = 27, 10.6 d J[C–P] = 26 $P(CH_3)_2Ph$
[Pd(**1**:3,4-η-C_4To_4Ph-(S_2CNMe_2)][b] (A)	147.4	*c*	123.0	103.4	140.8, 139.8, 137.7, 136.9, 136.0, 134.8, 134.5, 132.7, 130.3, 129.4, 128.7, 128.3, 127.2, 125.3	21.4, 21.2	208.8 $S_2CN(CH_3)_2$; 40.6, 39.7 $S_2CN(CH_3)_2$
[Pd(1:3,4-η-C_4To_4Ph)-(S_2CNEt_2)][b] 40 °C (B)	149.2 147.7	*c*	123.0	103.7 104.4	139.9, 137.7, 137.2, 137.0, 135.8, 134.7, 132.6, 132.5, 132.0, 130.6, 129.4, 129.9, 129.7, 129.6, 129.2, 127.9, 127.2, 125.3	21.3, 21.1	207.7 $S_2CN(CH_2CH_3)_2$; 46.0, 44.7 $S_2CN(CH_2CH_3)_2$; 12.7, 12.4 $S_2CN(CH_2CH_3)_2$
[Pd(1:3,4-η-C_4To_4Ph)-(S_2CN-*i*-Pr_2)][a] 60 °C (C)	150.1 149.9	*c*	123.9	108.5 107.5	144.1, 141.1, 140.9, 140.2, 138.5, 138.0, 137.1, 136.3, 135.7, 135.4, 134.7, 133.7, 132.3, 131.1, 130.7, 130.5, 128.9, 128.5, 128.1, 127.8, 127.2, 126.8, 125.3	21.2	208.2 $S_2CN\{CH(CH_3)_2\}_2$; 52.1, 51.0 $S_2CN\{CH(CH_3)_2\}_2$; 20.3, 20.1 $S_2CN\{CH(CH_3)_2\}_2$
60 °C				103.2 102.8 102.3 102.0			53.5, 50.3 broad $S_2CN\{CH(CH_3)_2\}_2$
-70 °C[b]	149.9 149.7 149.3 147.4		122.1 121.6			21.4	205.5, 205.2 $S_2CN\{CH(CH_3)_2\}_2$; 20.3, 19.9, 19.1 $S_2CN\{CH(CH_3)_2\}_2$
[Pd(1-3-η-C_4To_4OMe)-(S_2CNMe_2)][b] exo-OMe	89.6	125.5	89.6	88.3	139.9, 138.4, 137.8, 137.6, 132.6, 129.5, 129.2, 128.8, 128.7, 128.4, 128.0	21.5, 21.0	210.7 $S_2CN(CH_3)_2$; 40.9 $S_2CN(CH_3)_2$; 52.1 OCH_3

[a] In $CDCl_3$. [b] In CD_2Cl_2. [c] Indistinguishable from aromatics. [d] Doublet. [e] Insufficiently soluble to record spectrum. m, multiplet; t, triplet; q, quartet.

Table II. ^{1}H NMR Spectra at 100 MHz in $CDCl_3$ (Chemical Shifts, δ, in ppm; Coupling Constants in Hz; Relative Intensities in Parentheses)

Compd	Aromatics	*p*-Tolyl methyl	Other
[Pd(1-3-η-C_4To$_4$Ph)Cl]$_2$ (**10**)	6.78–7.74 m (21)	2.10 (6), 2.18 (3), 2.40 (3)	
[Pd(1-3-η-C_4To$_4$OMe)Cl]$_2$ (endo-OMe) (**11**)	6.85–8.00 m (16)	2.10 (6), 2.25 (3), 2.45 (3)	4.27 (3) OCH_3
[Pd(1-3-η-C_4To$_4$OMe)Cl]$_2$ (exo-OMe) (**12**)	6.84–7.98 m (16)	2.16 (6), 2.41 (6)	3.34 (3) OCH_3
[Pd(1-3-η-C_4To$_4$Ph)(PMe_2Ph)Cl][a] (**13a**)	6.70–7.92 m (26)	2.13 (3), 2.16 (3), 2.23 (3), 2.35 (3)	0.86 d (3) J[H-P] = 10, 1.22 d (3) J[H-P] = 10 } $P(CH_3)_2Ph$
[Pd(1-3-η-C_4To$_4$Ph{$P(OMe)_3$}Cl] (**13b**)	6.85–7.84 m (21)	2.16 (3), 2.18 (3), 2.22 (3), 2.38 (3)	3.24 d (9) J[H-P] = 13 $P(OCH_3)_3$
[Pd(1-3-η-C_4To$_4$Ph)(PMe_2Ph)$_2$]PF_6 (**14a**)	6.62–7.74 m (26)	2.20 (9), 2.46 (3)	0.82, t (6) N[H-P] = 10, 1.06 t (6) N[H-P] = 10 } $P(CH_3)_2Ph$
[Pd(1-3-η-C_4To$_4$Ph){$P(OMe)_3$}$_2$]PF_6[a] (**14b**)	6.95–7.86 m (21)	2.22 (9), 2.46 (3)	3.30 t (18) N[H-P] = 12 $P(OCH_3)_3$
[Pd(1-3-η-C_4To$_4$Ph)(COD)]PF_6[a] (**14c**)	7.02–7.82 m (21)	2.23 (6), 2.25 (3), 2.45 (3)	5.06 m (2), 5.51 m (2) CH, 1.63 (2) CH_2[b] } COD
[Pd(1-3-η-C_4To$_4$Ph)(bpy)]PF_6[a] (**14d**)	7.08–8.41 m (29)	2.28 (9), 2.40 (3)	bpy[c]
[Pd(1-3-η-C_4To$_4$Ph)(acac)] (**15**)	6.91–7.60 m (21)	2.21 (6), 2.23 (3), 2.30 (3)	1.76 (6) $(CH_3CO)_2CH$; 5.02 (1) $(CH_3CO)_2CH$
[Pd(1-3-η-C_4To$_4$Ph)(hfacac)] (**16**)	6.95–7.54 m (21)	2.22 (6), 2.26 (3), 2.34 (3)	5.75 (1) $(CF_3CO)_2CH$
[Pd(1-3-η-C_4To$_4$Ph)(S_2CNMe_2)] (**17a**)	6.82–7.66 m (21)	2.16 (6) 2.22 (3), 2.30 (3)	3.16 (6) $S_2CN(CH_3)_2$
[Pd(1-3-η-C_4To$_4$Ph)(S_2CNEt_2)] (**17b**)	6.80–7.69 m (21)	2.18 (6), 2.24 (3), 2.32 (3)	1.11 t (6) J[H-H] = 7 $S_2CN(CH_2CH_3)_2$; 3.63 q (4) J[H-H] = 7 $S_2CN(CH_2CH_3)_2$
[Pd(1-3-η-C_4To$_4$Ph)(S_2CN-*i*-Pr_2)] (**17c**)	6.84–7.68 m (21)	2.17 (6), 2.23 (3), 2.31 (3)	1.29 d (12) J[H-H] = 7 $S_2CN\{CH(CH_3)_2\}_2$; 4.55 m (2) $S_2CN\{CH(CH_3)_2\}_2$
[Pd(η^1-C_4To$_4$Ph)(acac)(PMe_2Ph)][a] (**18**)	6.44–7.42 m (26)	2.05 (3), 2.09 (3), 2.11 (3), 2.12 (3), 2.28 (3)[e]	1.81 (3)[e] $(CH_3CO)_2CH$; 5.32 (1) $(CH_3CO)_2CH$ 0.91 d (3) J[H-P] = 12, 1.08 d (3) J[H-P] = 11 $P(CH_3)_2Ph$
[Pd(η^1-C_4To$_4$Ph)(S_2CNMe_2)$P(OMe)_3$] (**19a**)	6.36–7.44 m (21)	2.01 (3), 2.09 (3), 2.15 (3), 2.20 (3)	3.22 (3), 3.37 (3) $S_2CN(CH_3)_2$; 3.17 d (9) J[H-P] = 14 $P(OCH_3)_2$
[Pd(η^1-C_4To$_4$Ph)(S_2CNMe_2) PEt_3] (**19b**)	6.47–7.52 m (21)	2.05 (3), 2.09 (3), 2.18 (3), 2.22 (3)	3.31 (3), 3.45 (3) $S_2CN(CH_3)_2$ 0.50–1.25 m (15) $P(CH_2CH_3)_3$
[Pd(η^1-C_4To$_4$Ph)(S_2CN-*i*-Pr_2)PMe_2Ph][a] (**19c**)	6.42–7.55 m (21)	2.05 (3), 2.08 (3), 2.13 (3), 2.27 (3)	1.33 br (6), 1.58 br (6) $S_2CN\{CH(CH_3)_2\}_2$; 4.74 m (2) $S_2CN\{CH(CH_3)_2\}_2$; 0.91 d (6) J[H-P] = 9, 0.97 d (6) J[H-P] = 10 $P(CH_3)_2Ph$
[Pd(η^1-C_4To$_4$Ph)(S_2CN-*i*-Pr_2)PMe_2Ph][a] (**19c + 22c**	6.44–7.60 m (42)	2.04 (3), 2.05 (3), 2.08 (3), 2.13 (6), 2.17 (3), 2.27 (3), 2.28 (3)	1.34 br (12), 1.59 br (12) $S_2CN\{CH(CH_3)_2\}_2$; 4.76 m (4) $S_2CN\{CH(CH_3)_2\}_2$; 0.91 d (6) J[H-P] = 9, 0.97 d (6) J[H-P] = 10 $P(CH_3)_2Ph$
[Pd(1:3,4-η-C_4To$_4$Ph)(S_2CNMe_2)] (A)	6.44–7.86 m (42)	2.12 (6), 2.23 (15), 2.29 (3)	3.20 (6), 3.23 (6) $S_2CN(CH_3)_2$
[Pd(1:3,4-η-C_4To$_4$Ph)(S_2CNEt_2)][a,f] (B)	6.40–7.87 m (42)	2.11 (6), 2.22 (15), 2.30 (3)	1.19 m (12) $S_2CN(CH_2CH_3)_2$; 5.67 m (8) $S_2CN(CH_2CH_3)_2$
[Pd(1:3,4-η-C_4To$_4$Ph)(S_2CN-*i*-Pr_2)][a] (C)	6.43–7.82 m (42)	2.07 (6), 2.18 (15), 2.25 (3)	1.30 br (24) $S_2CN\{CH(CH_3)_2\}_2$; 4.59 m (4) $S_2CN\{CH(CH_3)_2\}_2$
a,g	6.62–8.22 m (42)	2.04 (3), 2.05 (3), 2.08 (3), 2.13 (6), 2.17 (3), 2.27 (3), 2.28 (3)	0.95 br (24) $S_2CN\{CH(CH_3)_2\}_2$; *h*
−70 °C[a,f]	6.37–8.05 m (42)	2.15 (6), 2.24 (15), 2.35 (3)	1.14 m (12), 1.48 br (6), 1.59 d (3) J[H-H] = 7 1.64 d (3) J[H-H] = 7 $S_2CN\{CH(CH_3)_2\}_2$ 3.85 m (2), 5.10 m (1) $S_2CN\{CH(CH_3)_2\}_2$
−70 °C[a,g]			2.70 m (2), 4.95 m (1), 5.32 m (1) $S_2CN\{CH(CH_3)_2\}_2$
[Pd(1-3-η-C_4To$_4$OMe)(S_2CNMe_2)] (exo-OMe)	7.00–7.84 m (16)	2.16 (6), 2.30 (3), 2.33 (3)	3.23 (6) $S_2CN(CH_3)_2$; 3.49 (3) OCH_3

[a] At 220 MHz. [b] Other CH_2 resonances obscured by methyl signals. [c] bpy resonances included in aromatics. [d] Doublet. [e] One $(CH_3CO)_2CH$ resonance indistinguishable from *p*-tolyl methyls. [f] In CD_2Cl_2. [g] In toluene-d_8. [h] $S_2CN\{CH(CH_3)_2\}_2$ resonance merged into baseline. m, multiplet; t, triplet; q, quartet; br, broad.

Table III. Analytical Data (Calculated Values in Parentheses), Yields, and Decomposition Points

Complex	C, %	H, %	Other, %	Mol wt	Mp, °C dec
$[Pd(C_4To_4Ph)Cl]_2$ (**10**)	72.3 (72.2)	5.5 (5.3)	Cl, 6.0 (5.6)	1196 (1264)	>150
$[Pd(C_4To_4OMe)Cl]_2$ (**11**)	68.0 (67.7)	5.5 (5.3)	Cl, 6.2 (6.1)		198–199
$[Pd(C_4To_4OMe)Cl]_2$ (**12**)	68.3 (67.7)	5.6 (5.3)			182–184
$[Pd(C_4To_4Ph)(PMe_2Ph)Cl]$ (**13a**)	71.1 (71.8)	6.0 (5.7)	Cl, 4.9 (4.6)	728 (770)	>130
$[Pd(C_4To_4Ph)\{P(OMe)_3\}Cl]$ (**13b**)	64.8 (65.2)	5.8 (5.6)	Cl, 4.9 (4.7)		155–158
$[Pd(C_4To_4Ph)(PMe_2Ph)_2]PF_6$ (**14a**)	63.1 (63.7)	5.6 (5.4)			153–158
$[Pd(C_4To_4Ph)\{P(OMe)_3\}_2]PF_6 \cdot 0.5CH_2Cl_2$[a] (**14b**)	52.4 (51.8)	5.2 (5.0)			130–135
$[Pd(C_4To_4Ph)(cod)]PF_6$ (**14c**)	64.8 (65.0)	5.6 (5.3)			165–170
$[Pd(C_4To_4Ph)(bpy)]PF_6$ (**14d**)	64.4 (64.2)	4.8 (4.6)	N, 3.0 (3.1)		175–180
$[Pd(C_4To_4Ph)(acac)] \cdot Et_2O$ (**15**)	73.4 (73.4)	6.5 (6.5)			130–135
$[Pd(C_4To_4Ph)(CF_3COCHCOCF_3)]$ (**16**)	64.3 (64.3)	4.0 (4.2)			>120
$[Pd(C_4To_4Ph)(S_2CNMe_2)]$ (**17a**)	68.5 (68.7)	5.6 (5.5)	N, 2.0 (2.0)		168–170
$[Pd(C_4To_4Ph)(S_2CN\text{-}i\text{-}Pr_2)]$ (**17c**)	69.7 (70.0)	6.0 (6.1)	N, 1.5 (1.8)	767 (772)	150–155
$[Pd(C_4To_4Ph)(acac)(PMe_2Ph)]$ (**18**)	73.3 (73.5)	6.3 (6.1)			>100
$[Pd(C_4To_4Ph)(S_2CNMe_2)\{P(OMe)_3\}]$ (**19a**)	62.5 (62.9)	5.7 (5.7)	N, 1.7 (1.7) S, 8.3 (7.6)		>180
$[Pd(C_4To_4Ph)(S_2CNMe_2)(PEt_3)] \cdot MeOH$[a] (**19b**)	66.4 (66.2)	6.8 (6.7)	N, 1.9 (1.6)		>180
$[Pd(C_4To_4Ph)(S_2CN\text{-}i\text{-}Pr_2)(PMe_2Ph)]$ (**19c**)	69.3 (69.9)	6.7 (6.4)	N, 1.2 (1.5) S, 7.0 (7.0)	871 (911)	165–175
$[Pd(C_4To_4Ph)(S_2CNMe_2)] \cdot 0.25CH_2Cl_2$[a] (A)	67.0 (67.2)	5.7 (5.4)	N, 1.8 (1.9) S, 8.8 (8.7)	670 (737)	>160
$[Pd(C_4To_4Ph)(S_2CNEt_2)]$ (B)	69.0 (69.4)	5.8 (5.8)	N, 1.8 (1.9) S, 8.5 (8.6)		160–165
$[Pd(C_4To_4Ph)(S_2CN\text{-}i\text{-}Pr_2)]$ (C)	69.7 (70.0)	6.2 (6.1)	N, 1.8 (1.8) S, 8.4 (8.3)	761 (772)	155–160
$[Pd(C_4To_4Ph)(S_2CN\text{-}i\text{-}Pr_2)(PMe_2Ph)]$ (**19c + 22c**)	69.5 (69.9)	6.5 (6.4)	N, 1.4 (1.5) S, 7.1 (7.0)	906 (911)	165–170
$[Pd_2(Ph_2PCH_2PPh_2)_2Cl_2] \cdot 0.5CH_2Cl_2$[a] (**28**)	55.8 (55.4)	4.3 (4.1)	Cl, 10.4 (9.7)		>200

[a] Solvent of crystallization shown to be present by NMR spectroscopy.

CH_2Cl_2 (7 mL) and acetone (1 mL). The solution turned yellow-brown with the formation of the solvent complex $[Pd(C_4To_4Ph)(acetone)_2]PF_6$ and AgCl was precipitated. The mixture was quickly filtered under suction through Kieselguhr, into a stirred solution of 1,5-cod (1000 μL, 0.8 mmol) in CH_2Cl_2 (5 mL). After treating with activated charcoal, the mixture was filtered and reduced in volume; addition of ether caused crystallization. Recrystallization from CH_2Cl_2/ether gave **14c** as gold-colored crystals, yield 0.52 g (76%).

The complexes $[Pd(1\text{-}3\text{-}\eta\text{-}C_4To_4Ph)(PPhMe_2)_2]PF_6$ (**14a**), $[Pd(1\text{-}3\text{-}\eta\text{-}C_4To_4Ph)\{P(OMe)_3\}_2]PF_6$ (**14b**), and $[Pd(1\text{-}3\text{-}\eta\text{-}C_4To_4Ph)((bpy)]PF_6$ (**14d**) were prepared in 49, 75, and 72% yield, respectively, by addition of the appropriate ligand to the solution of $[Pd(C_4To_4Ph)(acetone)_2]PF_6$ prepared as above.

[Pd(1-3-η-C$_4$To$_4$Ph)(acac)] (15). Tl(acac) (0.79 g, 2.6 mmol) was added slowly to a stirred solution of complex **10** (1.5 g, 1.2 mmol) in CH_2Cl_2 (40 mL) at 0 °C. After 15 min the solvent was removed and the residue extracted with ether. The ether extract was chromatographed on silica gel in ether and crystallized from ether/MeOH at 0 °C to give yellow crystals of the product, yield 1.3 g (70%). The hexafluoroacetylacetonate **16** was obtained analogously as yellow crystals in 70% yield.

[Pd(1-3-η-C$_4$To$_4$Ph)(S$_2$CNR$_2$)] (17). A solution of $NaS_2CNMe_2 \cdot 2H_2O$ (425 mg, 2.4 mmol) in acetone (60 mL) was added slowly to a stirred solution of complex **10** (1.5 g, 1.2 mmol) in CH_2Cl_2 (60 mL) at 0 °C. After removal of solvent the residue was extracted with dichloromethane, and this solution was purified by filtering through a column of silica gel. Crystallization from CH_2Cl_2/MeOH at 0 °C gave complex **17a** as orange crystals, yield 1.2 g (70%).

The diethyldithiocarbamate complex **17b** was prepared analogously; in this case the CH_2Cl_2 extract was filtered through alumina and the complex was crystallized first from CH_2Cl_2/hexane and then CH_2Cl_2/MeOH, yield 85%.

The diisopropyldithiocarbamate complex **17c** was prepared in the same way as **17b** and was crystallized from Et_2O/MeOH and then CH_2Cl_2/MeOH, yield 89%.

[Pd(η^1-C$_4$To$_4$Ph)(acac)(PMe$_2$Ph)] (18). PMe_2Ph (200 μL, 1.1 mmol) was added dropwise to a stirred solution of complex **15** (600 mg, 0.9 mmol) in CH_2Cl_2 (30 mL) at 0 °C. After 30 min the solvent was removed from the red solution, the residue was extracted in ether and chromatographed on silica gel to give the product **18** in the first yellow eluent. Crystallization from CH_2Cl_2/MeOH at 0 °C gave complex **18** as yellow crystals, yield 0.40 g (53%).

[Pd(η^1-C$_4$To$_4$Ph)(S$_2$CNMe$_2$)P(OMe)$_3$] (19a). A solution of $P(OMe)_3$ (90 μL, 0.8 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a stirred solution of $[Pd(C_4To_4Ph)(S_2CNMe_2)]$ (**17a**, 500 mg, 0.7 mmol) in CH_2Cl_2 (20 mL). After 15 min the solvent was removed and a CH_2Cl_2 extract of the product purified by chromatography on silica gel. Crystallization of the first yellow fraction from CH_2Cl_2/MeOH at 0 °C gave **19a** as pale yellow crystals, yield 0.38 g (65%).

[Pd(η^1-C$_4$To$_4$Ph)(S$_2$CNMe$_2$)PEt$_3$] (19b). A solution of PEt_3 (103 μL, 0.7 mmol) in CH_2Cl_2 (10 mL) was added slowly to a stirred solution of complex **17a** (0.7 mmol) in CH_2Cl_2 (20 mL). After 15 min the solvent was removed and the residue washed with ether and crystallized from CH_2Cl_2/MeOH at 0 °C to give complex **19b** as pale yellow crystals, yield 0.30 g (51%).

[Pd(η^1-C$_4$To$_4$Ph)(S$_2$CN-*i*-Pr$_2$)(PMe$_2$Ph)] (19c). PMe_2Ph (107 mg, 0.78 mmol) was added to a stirred solution of $[Pd(1\text{-}3\text{-}\eta\text{-}C_4To_4Ph)(S_2CN\text{-}i\text{-}Pr_2)]$ (**17**, 0.60 g, 0.78 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The solvent was removed in vacuo and the residue was chromatographed in ether on silica gel. Crystallization of the yellow eluate from CH_2Cl_2/MeOH gave complex **19c** as lemon yellow crystals, yield 0.56 g (71%).

[Pd(η^1-C$_4$To$_4$Ph)(acac)(PMe$_2$Ph)] (18) → [Pd(η^1-C$_4$To$_4$Ph)-(S$_2$CN-*i*-Pr$_2$)(PMe$_2$Ph)] (19c). A solution of $NaS_2CN\text{-}i\text{-}Pr_2 \cdot 2H_2O$ (140 mg, 0.6 mmol) in acetone (15 mL) was added dropwise to a solution of $[Pd(\eta^1\text{-}C_4To_4Ph)(acac)(PMe_2Ph)]$ (500 mg, 0.6 mmol) in CH_2Cl_2 (2 mL) and the mixture stirred for 0.5 h. After removal of solvent the product was extracted with a diethyl ether–petroleum ether mixture (1:2 v/v) and chromatographed over alumina eluting with the same mixture. Crystallization of the eluate from CH_2Cl_2/MeOH gave the product **19c** as lemon yellow crystals (280 mg, 51%).

[Pd(1:3,4-η-C$_4$To$_4$Ph)(S$_2$CNMe$_2$)] (A). $[Pd(1\text{-}3\text{-}\eta^3\text{-}C_4To_4Ph)(S_2CNMe_2)]$ (**17a**, 500 mg, 0.7 mmol) was refluxed in $CHCl_3$ (30 mL) for 2 h. After removal of solvent the crude product was chromatographed on silica gel in CH_2Cl_2 and the first red band was collected. Addition of ether to the red oil obtained on removal of solvent yielded the product as yellow microcrystals which were washed with ether and MeOH before drying, yield 0.29 g (58%).

[Pd(1:3,4-η-C$_4$To$_4$Ph)(S$_2$CNEt$_2$)] (B). A solution of complex **17b** (0.75 g, 1.0 mmol) in $CHCl_3$ (50 mL) was refluxed for 2 h. The red solution was evaporated to dryness and the residue chromatographed

in CH_2Cl_2 over silica gel. The orange eluate was crystallized first from ether/pentane and then from CH_2Cl_2/MeOH at 0 °C to give the product as orange crystals, yield 0.35 g (47%).

[Pd(1:3,4-η-C_4To_4Ph)(S_2CN-*i*-Pr_2)] (C). A solution of complex **17c** (0.5 g, 0.65 mmol) in $CHCl_3$ (40 mL) was refluxed for 1.5 h when it changed color from orange to red. After removal of solvent the residue was chromatographed in ether over alumina and the orange eluate was collected. The solvent was removed and the residue was crystallized from ether/pentane and then from CH_2Cl_2/MeOH to give the product as yellow crystals, yield 0.37 g (73%).

[Pd(η¹-C_4To_4Ph)(S_2CN-*i*-Pr_2)(PMe_2Ph)], Mixture of Isomers 19c and 22c. PMe_2Ph (107 mg, 0.78 mmol) was added to a stirred solution of [Pd(1:3,4-η-C_4To_4Ph)(S_2CN-*i*-Pr_2)] (0.60 g, 0.78 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The solvent was removed in vacuo and the residue extracted with ether. This solution was chromatographed in ether over alumina and the yellow eluate was taken to dryness and crystallized from CH_2Cl_2/MeOH to give the product as lemon-yellow crystals, yield 0.62 g (88%).

Reaction of [Pd(1-3-η-C_4To_4Ph)Cl]$_2$ with $Ph_2PCH_2PPh_2$ to Give 28. $Ph_2PCH_2PPh_2$ (0.12 g, 0.32 mmol) was added under N_2 to a degassed solution of [PdCl(1-3-η-C_4To_4Ph)]$_2$ (**10**, 0.20 g, 0.16 mmol) in chloroform (5 mL) and the solution was set aside at 20 °C. A green coloration slowly appeared and persisted for about 24 h. The solution was then evaporated to dryness and the residue washed with ether to remove soluble organic materials. The powder remaining was crystallized from CH_2Cl_2/petroleum ether at 0 °C to give brick-red crystals of the product: yield 0.11 g (68%); ^1H NMR spectrum (220 MHz) in $CDCl_3$ δ 4.14 (quintet, 4 H, CH_2, J(H-P) = 8 Hz), 7.14–8.05 (m 40 H, phenyl).

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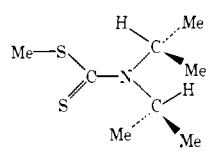
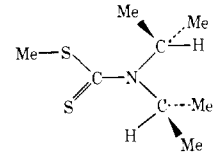
(14) Other workers have found that the isopropyl groups do have preferred conformations in diisopropyldithiocarbamate complexes of Ni,[15] Sn,[16] or Ti[17] and that their rotation is restricted by S···Me nonbonded interactions.[15,16] In addition, two rotamers (**23a** and **23b**) of MeSC(S)N(Pr-*i*)$_2$ are


23a


23b

frozen out and can be detected at −35 °C.[18] It is therefore most plausible that the low-temperature NMR spectra of the mixture **20c** + **21c** be interpreted in terms of each isomer existing as two rotamers which interconvert quickly on the NMR time scale at 60 °C. On this basis the number of isopropyl methyls in the frozen-out low-temperature form should be four for **20c** and four for **21c**, giving a total of eight resonances which are observed as doublets owing to coupling to the isopropyl CH's. At ambient temperature in the ^1H spectrum all are approximately coincident under a broad envelope at δ 1.30; at −70 °C in CD_2Cl_2 these are split into two sharp doublets (J = 7 Hz) at δ 1.59 and 1.64 (of approximately equal intensity 1), one broad resonance (δ 1.48, relative intensity 2), and an unresolved multiplet (δ 1.14, intensity 4). At −70 °C in toluene-d_8 the isopropyl CH resonances appear as multiplets at δ 5.32, 4.95, and 2.70 in the ratio 1:1:2. Rotation about the S_2C–N< bond is also possible but this is a higher energy process for which we have no evidence in these systems.
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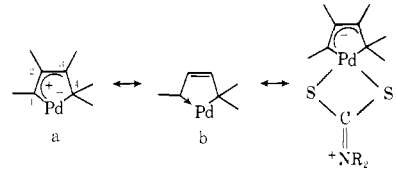
(24) We are indebted to Professor N. M. Atherton for measuring these spectra and for assisting us with their interpretation.
(25) The intensity ratios of the main multiplet expected for a nine-line spectrum are 1:8:28:56:70:56:28:8:1 and for an 11-line spectrum are 1:10:45:120:210:252:210:120:45:10:1.
(26) Other studies have shown that coupling to the ortho hydrogens is of the same order as that to *p*-methyl hydrogens; see, for example, A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Free Radicals", Academic Press, New York, N.Y., 1968, p 59.
(27) (a) K. MacKenzie, "The Chemistry of Alkenes", Vol. 1, S. Patai, Ed., Wiley-Interscience, New York, N.Y., 1964, p 391 ff; (b) *ibid.*, Vol. 2, 1970, p 115 ff.
(28) The intermediate (or transition state) (iii) may be represented by the canonical forms a–c; c is probably a very important contributor since the positive charge can be localized on the nitrogen, as shown.



a b c

(29) Although no data on the energetics of the stereomutation are available, a lower limit for $\Delta G^{\ddagger}$ of ca. 18.5 kcal mol^{-1} may be estimated from the fact that the two signals in the ^{13}C NMR spectrum due to C(1) in the isomer mixture (C) have not yet coalesced at the highest temperature (60 °C) that is attainable. If the stereomutation were fast enough on the NMR time scale only a single resonance would be observed.
(30) J. W. Faller and A. M. Rosan, *J. Am. Chem. Soc.*, **99**, 4859 (1977).
(31) R. G. Salomon, M. F. Salomon, and J. L. C. Kachinski, *J. Am. Chem. Soc.*, **99**, 1043 (1977).