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ortho-METALLATION REACTIONS OF PALLADIUM BIS(HEXAFLUOROACETYLACETONATE)

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Summary

ortho-Metallation reactions of palladium bis(hexafluoroacetylacetonate) [Pd(F_6acac)$_2$] have been studied by ^{1}H and ^{19}F NMR. *N,N'*-Dimethylbenzylamine produces a fluxional 1 : 1 adduct (*O*-F_6acac)(O_2-F_6acac)Pd(amine) which contains a η^1 oxygen-bonded F_6acac group. The ligands benzyl methyl sulfide and 4,4'-dimethoxythiobenzophenone produce 1 : 1 intermediates of the type (*C*-F_6acac)(O_2-F_6acac)Pd(ligand) which contain a carbon-bonded F_6acac group. These adducts spontaneously lose hexafluoroacetylacetone and undergo cyclopalladation at room temperature.

Metallation of azobenzene yields (PhN=NC_6H_4)Pd(F_6acac) and the doubly *ortho*-metallated compound (C_6H_4N=NC_6H_4)Pd$_2$(F_6acac)$_2$. Similar single metallations occur with benzylideneaniline and acetophenone oxime but thiobenzanilide gave [PhC(S)NPh]$_2$Pd and [PhC(S)NPh]Pd(F_6acac).

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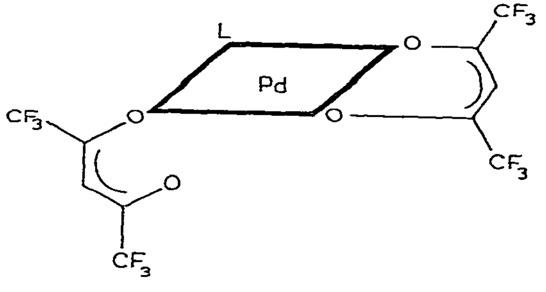
ortho-Metallation reactions are a broad class of aromatic substitution processes in which a coordinated organic ligand undergoes intramolecular metallation with the formation of a new metal—carbon σ bond [1,2,3]. In some cases, it has been shown that coordination compounds are formed as intermediates which subsequently cyclize. Among these may be mentioned [(PhO)$_3$P]$_3$RuHCl [4] and the thioketone complex Re$_2$(CO)$_9$(SCPh$_2$) [5]. Cyclopalladation of azobenzene appears to proceed by an electrophilic attack on the aryl ring [6]. Bis(azobenzene)palladium(II) chloride has been prepared [7,8] and its crystal structure described [9]. This compound may be involved in the *ortho*-metallation of azobenzene but, at room temperature, it is stable and does not spontaneously cyclize. Trofimenko [10] reported that the thioether complex (PhCH$_2$SMe)$_2$PdCl$_2$ did not react with Na$_2$PdCl$_4$ but the nitrogen complexes (PhCH$_2$NMe$_2$)$_2$PdCl$_2$ and (1-phenylpyrazole)$_2$PdCl$_2$ could be cyclometallated by additional tetrachloropalladate, leaving open the question of whether these compounds are in fact intermediates.

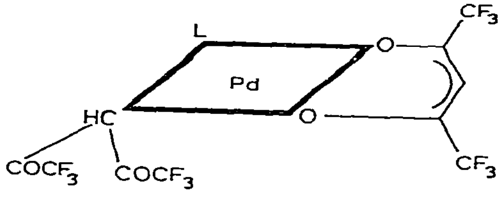
This paper describes synthetic and mechanistic studies of the *ortho*-metallation chemistry of palladium bis(hexafluoroacetylacetonate), $Pd(F_6acac)_2$, and the spectroscopic characterization of reactive intermediates in the metallation reactions. Use of $Pd(F_6acac)_2$ is convenient. The acid—base chemistry of this strong Lewis acid is now well defined. With molecular donors, it forms three classes of adducts of the type $Pd(F_6acac)_2(ligand)_n$ ($n = 1, 2, 4$) which may be described on the basis of stoichiometry. Representative members of the $n = 1$ and 4 classes have been characterized by X-ray crystallography [11]. In addition to having available a series of model compounds with which to compare proposed intermediates, ^{19}F nuclear magnetic resonance spectroscopy can be used to follow the course of $Pd(F_6acac)_2$ reactions. The *ortho*-palladation reactions of $Pd(F_6acac)_2$ are qualitatively much more rapid than those of $PdCl_4^{2-}$, one of the most commonly used reagents, presumably because of the highly electrophilic nature of the metal center. The hexafluoroacetylacetonate group which remains bonded to the metal imparts high solubility to the products, making them easy to purify and convenient intermediates for further synthetic reactions.

The *ortho*-metallation of *N,N*-dimethylbenzylamine was followed by ^1H and ^{19}F NMR. Equal amounts of 0.2 *M* solutions of the reactants in $CDCl_3$ were cooled to —78°C, mixed, and allowed to warm to room temperature in the probe of the NMR spectrometer. Formation of an adduct, I, at —78°C was rapid and no signals due to the starting materials were seen. Integration of the proton spectrum showed that I contained equimolar amounts of $Pd(F_6acac)_2$ and the amine. Spectral parameters for the adduct are δ 6.10 (F_6acac methine CH), 3.85 ($PhCH_2$) and 2.39 ppm (NCH_3). The ^{19}F NMR spectrum of I consisted of a single peak at 76.1 ppm. This indicates that the intermediate is a complex of the type (amine)$Pd(O\text{-}F_6acac)(O_2\text{-}F_6acac)$ which contains one bidentate and monodentate F_6acac, both bonded to palladium through the terminal oxygen atoms. The analogous triphenylphosphine derivative has been prepared and structurally characterized [11]; it is fluxional, and a similar, rapid interconversion of the $\eta^1\text{-}O\text{-}F_6acac$ and $\eta^2\text{-}O_2\text{-}F_6acac$ groups accounts for the single ^{19}F resonance [11].

The reaction of benzyl methyl sulfide and $Pd(F_6acac)_2$ at room temperature in $CDCl_3$ produced a 1 : 1 adduct IIa which contained one methine carbon-



(I, L = $PhCH_2NMe_2$)



(IIa, L = $PhCH_2SMe$,
IIb, L = $(p\text{-}MeOC_6H_4)_2CS$)

TABLE 1

ANALYTICAL DATA

Compound	m.p. (°C)	Found (calcd) (%)			
		C	H	N	S
III	163—165	35.0 (34.7)	2.2 (2.2)		7.3 (7.1)
IV	170	41.9 (42.1)	2.3 (2.5)		5.7 (5 6)
V	142—143	37.6 (37.3)	2.9 (2.8)	3.1 (3.0)	
VI	193	41.2 (41.1)	1.8 (1.9)	2.8 (3.0)	
VII	157	41.3 (41.3)	1.9 (2.0)	5.6 (5.7)	
VIII		32.7 (32.7)	1.4 (1.5)	3.4 (3.5)	
IX	203—205	44.1 (43.7)	2.8 (2 7)	5.4 (5.4)	
X	133—134	43.5 (43.8)	2.2 (2.2)	2.8 (2.8)	
XI	196—197	34.8 (34.9)	1.9 (2.0)	3.1 (3 1)	
XII	193	58.5 (58.9)	3.8 (3.8)	5.0 (5.3)	
XIII	146 (dec)	40.9 (41.1)	2.1 (2.1)	2.6 (2.7)	

bonded F_6acac and one bidentate oxygen-bonded F_6acac, i.e. $(PhCH_2SMe)Pd$-(C-F_6acac)(O_2-F_6acac). Integration of the proton spectrum confirmed the stoichiometry and the ^1H chemical shifts were δ 6.33 (O_2-F_6acac methine C—H), 5.24 (—$CH(COCF_3)_2$), 3.88 (apparent doublet, SCH_2) and 2.13 ppm (SCH_3). The ^{19}F NMR spectrum contained two singlets at 75.24 and 77.17 ppm assigned to the C-F_6acac and O_2-F_6acac groups, respectively. The proposed structure is supported by the infrared spectrum which showed a strong band at 1741 cm^{-1} in $CDCl_3$ due to the uncoordinated carbonyl groups in the CH-

TABLE 2

NMR SPECTRAL DATA

Compound	Nucleus δ (ppm)
III	^{19}F: 75.7, 76.2. ^1H: 7.4 (H *ortho* to Pd), 7.0 (phenyl), 6.11 (F_6acac), 4.29, 3.89 (J(AB) 14, SCH_2), 2.67 (SCH_3)
IV	^{19}F: 76.05, 76.13. ^1H: 7.58 (H *ortho* to Pd), 7.3—6.5 (aromatic), 6.09 (F_6acac), 3.89 (OCH_3)
V	^{19}F: 75.6, 76.6. ^1H: 7.1 (m, phenyl), 6.07 (F_6acac), 3.95 (NCH_2), 2.87 (NCH_3)
VI	^{19}F: 75.4, 76.3. ^1H: 8.42 (d, H *ortho* to N), 7—8 (aromatic), 6.08 (F_6acac).
VII	^{19}F: 75.5, 76.4. ^1H: 8.2—7.2 (aromatic), 6.10 (F_6acac).
IX	^{19}F: 75.6, 76.6. ^1H: 8.2—7.3 (aromatic), 6.20 (F_6acac), 2.45, 1.40 (CH_3).
X	^{19}F: 76.4, 75.4. ^1H: 8.00 (N=CH), 7.5—7.1 (aromatic), 6.8 (F_6acac)
XI [a]	^{19}F: 74.4. ^1H: 11.3 (N—OH), 7.5—7.1 (aromatic), 5.94 (F_6acac), 2.36 (CH_3).
XIII	^{19}F: 75.0, 74.4. ^1H' 7.6—6.6 (aromatic), 6.14 (F_6acac).

[a] In DMSO-d_6.

TABLE 3

ELECTRONIC SPECTRAL DATA

Compound	Solvent	λ_{max} (nm) (log ϵ)
III	$CHCl_3$	280(4.30), 297(4.31), 330(4.30)
IV	$CHCl_3$	298(3.95), 325(3.91), 511(3.80)
V	$CHCl_3$	317(2.72)
VI	$CHCl_3$	263(4.37), 3.05(3.95), 317(4.00), 340(3.90)
VII	$CHCl_3$	330(4.15), 365(sh, 4.06), 385(sh, 3.97), 445(3.63), 475(sh, 3.53)
VIII	Nujol	400, 570, 620
IX	$CHCl_3$	335(4.23), 452(4.67)
X	$CHCl_3$	300(4.06), 322(sh), 336(4.06)
XI	$CHCl_3$	285(3.85), 306(3.86), 340(sh)
XII	CH_3CN	275(4.65), 355(3.73), 470(sh)
XIII	CH_3CN	250(4.46), 280(4.40)

$(COCF_3)_2$ ligand and a 1670 cm^{-1} group mode absorption associated with the O_2-F_6acac moiety. Addition of more $PhCH_2SMe$ caused the two ^{19}F resonances to coalesce into a broad (*w*/2 88 cps) peak at 76.1 ppm when the sulfide : Pd ratio was 10 : 1. A structurally similar adduct, IIb, was formed from Pd$(F_6acac)_2$ and 4,4'-dimethoxythiobenzophenone. It showed ^{19}F resonances at δ 74.85, 75.50 and 77.00 ppm; here, the nonequivalent CF_3 groups in the O_2-F_6acac unit were resolved. The ^1H chemical shifts were δ 6.05, (O_2-F_6acac), 5.26 (C-F_6acac) and 3.96 ppm (OCH_3) and ν(CO) was 1738 cm^{-1}.

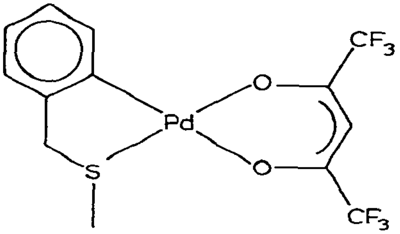
Adducts IIa and IIb lose hexafluoroacetylacetone on standing in $CDCl_3$ solu-

TABLE 4

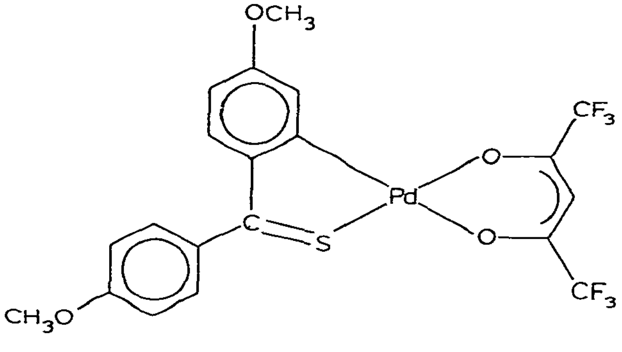
INFRARED SPECTRAL DATA

Compound	ν_{max} (cm^{-1})
III	3020w, 1640s, 1555m, 1480m, 1470s, 1455s, 1370m, 1340m, 1260vs, 1200vs, 1165vs, 1100s, 795s, 750s, 740s, 685s, 590w, 430m
IV	3020w, 1640s, 1585s, 1560m, 1475s, 1360s, 1350s, 1210vs, 1160vs, 1135vs, 1105s, 1025s, 870m, 840m, 820s, 795s, 685m, 625m
V	3020w, 1640s, 1580m, 1550s, 1520s, 1445s, 1405s, 1345m, 1260vs, 1205vs, 1150vs, 1100s, 1050m, 985m, 860m, 815m, 815m, 790s, 735s, 685s, 590m
VI	3025w, 1640s, 1610m, 1585m, 1550m, 1490s, 1455s, 1445m, 1380m, 1265vs, 1220vs, 1205s, 1155vs, 1130vs, 1100s, 785s, 750s, 735s, 685s, 590w, 410m
VII	3030w, 1640s, 1585m, 1550s, 1485s, 1345m, 1270vs, 1200vs, 1150vs, 1100m, 790s, 765s, 750m, 690m
VIII	3100w, 1640s, 1570m, 1555s, 1470s, 1450m, 1350m, 1275s, 1260s, 1225vs, 1205s, 1150vs, 1105s, 795s, 765s, 745m, 680m
IX	3030w, 1640s, 1580m, 1555m, 1480m, 1370m, 1355m, 1260vs, 1210vs, 1150vs, 1105s, 810s, 790s, 745m, 685s
X	3030w, 1640s, 1585m, 1550m, 1480m, 1345w, 1265vs, 1200vs, 1155vs, 1100m, 790s, 765s, 715m, 690s
XI	3510m, 3480w, 1625s, 1595m, 1580m, 1555s, 1475s, 1380s, 1330s, 1255vs, 1210vs, 1155vs, 1095s, 800s, 755s, 720m, 685s, 595m, 490m
XII [a]	3025w, 1590s, 1590s, 1515s, 1480s, 1445m, 1225s, 1070m, 1025m, 1000s, 775s, 745s, 715s, 685s, 605m
XIII [a]	3030w, 1625s, 1590m, 1550m, 1515s, 1470m, 1340m, 1255vs, 1210vs, 1150vs, 1095m, 1000m, 780m, 755m, 720s, 685s

[a] In KBr.



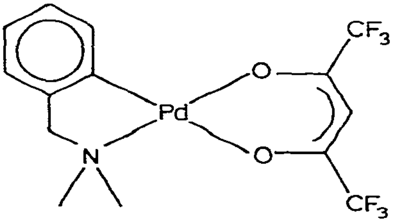
(III)



(IV)

tion at room temperature to yield the *ortho*-metallated compounds III and IV. The thioketone derivative IV is bright orange and its electronic spectrum contained a band at 511 nm attributed to ligand → metal charge transfer. The greater reactivity of these 1 : 1 Pd(F_6acac)$_2$ adducts may be contrasted with that of ($PhCH_2SMe$)$_2$$PdCl_2$ [10] and [(4-MeOPh)$_2$CS]$_2$$PdCl_2$ [12] which do not undergo spontaneous *ortho*-metallation.

Metallation of I to form V was even more rapid and, in the NMR experiments, was complete after about 30 minutes at room temperature. If excess benzyldimethylamine was added as a proton acceptor, the salt $PhCH_2NMe_2H^+$-F_6acac$^-$ was produced. In chloroform, this salt had δ ^{1}H at 5.88 (F_6acac$^-$), 4.20 (NCH_2) and 2.75 (NCH_3). Similarly, 2-phenylpyridine eliminated hexafluoroacetylacetone at room temperature to form VI and the intermediate adduct could not be definitely characterized. Because of the facile succeeding cyclization reactions, preparative scale experiments to isolate pure samples of I, IIa and IIb failed.



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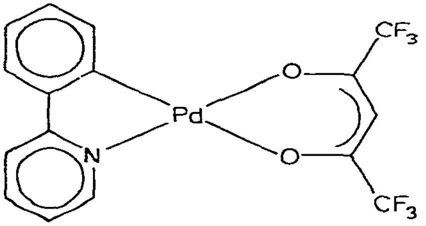
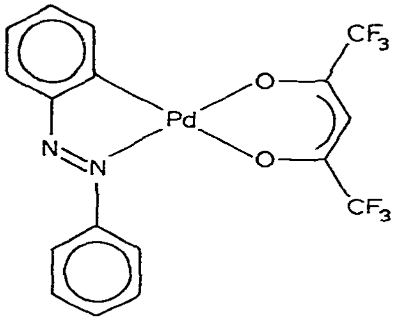


(VI)

No complex formation between Pd(F_6acac)$_2$ and azobenzene could be detected by ^{19}F NMR spectroscopy. However, this compound underwent a clean *ortho*-metallation in refluxing toluene to produce phenylazophenylpalladium hexafluoroacetylacetonate, VII, and the unusual doubly *ortho*-metallated azobenzene derivative VIII.

Compound VII crystallized readily from hydrocarbon solvents, and, on heating, the crystals underwent a solid state rearrangement which will be described in



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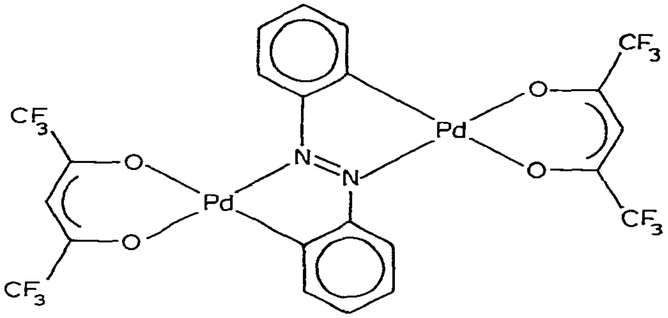


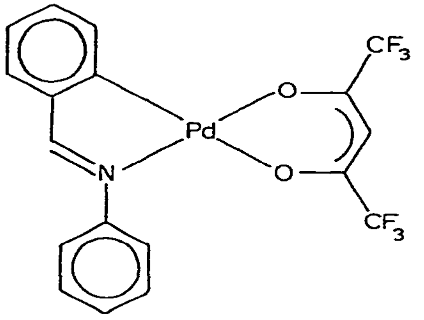
(VIII)

detail elsewhere [13]. Its Raman spectrum in chloroform exhibited a polarized, resonance enhanced N=N stretching band at 1386 cm^{-1}. This is in good agreement with the 1348 cm^{-1} scattering in $IrHCl(C_6H_4N{=}NPh)(PPh_3)_2$ and represents a significant shift from the corresponding band at 1442 cm^{-1} in pure azobenzene [14]. The purple, crystalline dipalladium compound VIII was insoluble in common organic solvents and was characterized by its elemental analysis and the mass spectrum, which demonstrated a parent ion at *m/e* 806 and $[P - F_6acac]^+$ at *m/e* 598. The electronic spectrum, obtained on a Nujol mull, was quite different from the spectra of the other *ortho*-metallated compounds described in this paper, c.f. Table 3, and contained absorptions at 570 and 620 nm. The presence of such low energy bands may indicate that molecules of VIII are stacked in the solid state in such a way that significant Pd—Pd interactions occur. A similar effect was observed by Balch and coworkers [15], and independently by us, in pyrazine$[Rh(CO)_2Cl]_2$ which presumably oligomerizes in the solid through metal—metal bonds. Metallation of azotoluene with $Pd(F_6acac)_2$ afforded IX, the 4,4′-dimethyl analogue of VII but the corresponding bimetallic derivative was not obtained in analytically pure form.

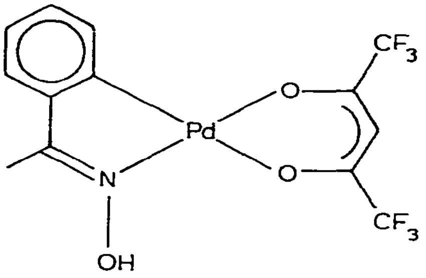
The yield of VII relative to VIII is much higher when the reaction is carried out in refluxing butyronitrile instead of toluene. This may be due to the formation of a weak complex between the nitrile and $Pd(F_6acac)_2$ which is less reactive than $Pd(F_6acac)_2$ itself. In support of this, it was found that the carbonyl stretching band in $Pd(F_6acac)_2$ shifted from 1603 cm^{-1} in chloroform or Nujol to 1685 cm^{-1} in acetonitrile solvent. This is indicative of weak complex formation for no solid adduct was obtained upon evaporation of the acetonitrile solutions.

Benzylidene aniline was metallated by $Pd(F_6acac)_2$ in refluxing toluene to provide X. Aryl oximes are also known to participate in *ortho*-metallation reactions [16]. Such a reaction was observed with acetophenone oxime and an alternate possibility, loss of the hydroxyl proton as hexafluoroacetylacetone, did not occur. The hydroxyl group in the metallated product XI remained intact as evidenced by the OH stretching vibration at 3510 cm^{-1} and the 11.3 ppm peak in the ^1H NMR spectrum.

Elimination of the acidic N—H proton in thiobenzanilide, however, led to

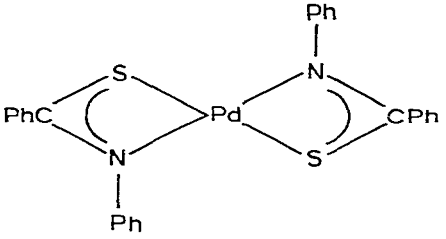


(X)

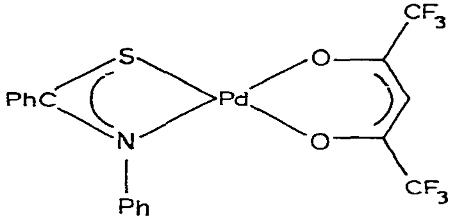


(XI)

the formation of the palladium(II) chelates XII and XIII. Purification of XIII was aided by its relatively high solubility in hydrocarbons. Neither compound exhibited the N—H stretching band found in the starting material. In principle,



(XII)



(XIII)

XII could exist as either a *cis* or *trans* isomer and there is no experimental evidence at hand which distinguishes between the two. However, the *trans* configuration is preferred, since in it steric repulsion between the two *N*-phenyl rings is minimized.

Experimental

The organic compounds used in this work were available commercially. Palladium bis(hexafluoroacetylacetonate) was prepared from Na_2PdCl_4 and sodium hexafluoroacetylacetonate in water and purified by vacuum sublimation. ^1H and ^{19}F NMR spectra were obtained at 100 and 94.1 MHz respectively and were referenced to internal $(CH_3)_4Si$ or $CFCl_3$. Infrared spectra were obtained on Nujol mulls (unless otherwise noted) using a spectrometer with grating optics; estimated precision of peak maxima is ± 5 cm^{-1}. Mass spectra were obtained in the electron impact mode using 70 eV electrons. Electronic spectra were recorded on a Cary 14 spectrometer. Analytical and spectroscopic data for the new compounds reported in this paper are given in Tables 1—4.

Metallation of 4,4'-dimethoxythiobenzophenone

Palladium hexafluoroacetylacetonate (0.52 g, 1 mmol) and the thioketone (1 mmol, 0.25 g) were dissolved in 25 ml benzene. After refluxing overnight, the orange reaction mixture was filtered to remove some tar and taken to dryness. Recrystallization from dichloromethane-hexane gave a gummy solid which was twice recrystallized from hot hexane to give 0.30 gm (52%) of the metallated thioketone IV as fibrous, bright orange needles.

Metallation of 2-phenylpyridine

2-Phenylpyridine (1 mmol, 0.16 g) and 0.52 g (1 mmol) Pd(F_6acac)$_2$ in 10 ml benzene were refluxed and stirred overnight. The solvent was stripped and the residue recrystallized from toluene-heptane to afford 0.37 g (80%) of VI as yellow needles.

Cyclopalladation of azobenzene

A. In toluene. Azobenzene (0.72 g, 4 mmol), Pd(F_6acac)$_2$ (2.08 g, 4 mmol) and 35 ml toluene were refluxed and stirred overnight. Filtration of the reaction mixture yielded 0.65 g of VIII as tiny, dark purple needles. The filtrate was rapidly passed through a 4" × 0.5" Florisil column to remove traces of palladium metal and other impurities; the column was then washed with fresh solvent to elute product which remained on the column. The combined toluene solutions were taken to dryness on a rotary evaporator. Recrystallization of the material remaining gave 0.40 g of yellow needles of VII.

B. Butyronitrile solvent. A mixture of 4 mmol of each reactant and 50 ml butyronitrile was stirred and refluxed overnight. Filtration afforded 0.16 g of VIII. Butyronitrile was removed from the filtrate under reduced pressure. The residue was quickly chromatographed on Florisil as described above. After recrystallization from hexane, the yield of VII was 1.40 g.

ortho-Metallation of acetophenone oxime

One mmol each of acetophenone oxime and Pd(F_6acac)$_2$ in 20 ml benzene was refluxed for 16 hours. The reaction mixture was reduced to a small volume with a nitrogen jet to obtain the crude product. An additional recrystallization from benzene gave 0.31 g (69%) of yellow crystalline XI.

Reaction of Palladium bis(hexafluoroacetylacetonate) with thiobenzanilide

A mixture of 0.52 g (1 mmol) Pd(F_6acac)$_2$, 0.36 g (2 mmol) thiobenzanilide and 20 ml toluene was refluxed for five minutes. The reaction mixture was cooled and the toluene removed under reduced pressure. The residue was extracted with 30 ml hot hexane. The extract was evaporated to a small volume and chilled to provide 0.04 g of XIII as red nodules. Recrystallization of the hexane-insoluble material from benzene-cyclohexane gave 0.10 g of XII as brown needles.

Acknowledgements

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