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SYNTHESES AND CHARACTERIZATION OF NEW PALLADIUM(II) COMPLEXES WITH FUNCTIONALLY SUBSTITUTED CYCLOPENTADIENYL GROUPS

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Summary

Thallium [1-(*p*-tolylimino)-2-methylpropyl]cyclopentadienide, $Tl[C_5H_4C(=NC_6H_4CH_3)CH(CH_3)_2]$, was prepared and treatment of the salt with $[\{PdCl_2(PREt_2)\}_2]$ (R = Ph and Et) yielded mononuclear palladium(II) complexes, $[Pd\{\eta^5\text{-}C_5H_4C(=NC_6H_4CH_3)CH(CH_3)_2\}Cl(PREt_2)]$, with an imidoyl-substituted η^5-cyclopentadienyl group. In addition, $[Pd(\eta^5\text{-}C_5H_4\text{-}COY)Cl(PPhEt_2)]$ ($Y = CH_3$ and OCH_3) complexes were obtained from the sodium salts of their substituted cyclopentadienyl groups. These new compounds were characterized by means of ^1H and ^{13}C NMR and IR spectroscopy.

Introduction

Functionally substituted ligands in transition metal organometallics have received considerable interest in view of: (i) the anchoring of homogeneous organometallic species by bonding chemically with silica gels and polymers [1]; (ii) linking two or more metal centers to form bimetallic or cluster complexes with sophisticated catalytic activity [2]; and (iii) the introduction of chirality into the compounds with the aid of the functional substituents [3]. Aromatic-type electrophilic substitution reactions were useful for functionalization of the η^5-cyclopentadienyl rings in $[M(\eta^5\text{-}C_5H_5)_2]$ (M = Fe, Ru, Os), $[M(\eta^5\text{-}C_5H_5)(CO)_3]$ (M = Mn, Tc, Re), $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$, and $[Cr(\eta^5\text{-}C_5H_5)(CO)_2(NO)]$ [4]. However, similar functionalization of other types of η^5-cyclopentadienyl transition metal complexes has been impeded due to their inherent lack of aromatic character or to other more facile reaction pathways that take place under the reaction conditions involved [4]. Accordingly, it would be worthwhile to develop new mild reagents of functionally substituted cyclopentadienyl groups, such as thallium salts, for the syntheses of transition metal derivatives [4].

In the present paper, we report the syntheses and characterization of chloro(func-

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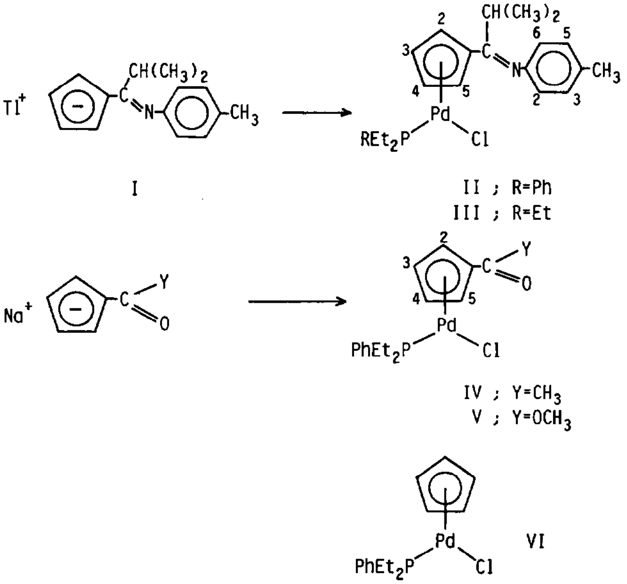
tionally substituted η^5-cyclopentadienyl)(tertiary phosphine)palladium(II) complexes derived from thallium [1-(*p*-tolylimino)-2-methylpropyl]cyclopentadienide (I) and sodium acetyl-and methoxycarbonylcyclopentadienides. The present work seems to be the first example of palladium complexes with functionally substituted cyclopentadienyl groups.



SCHEME 1

Results and discussion

An imidoyl chloride, *N*-1-(2-methyl-1-chloropropylidene)-*p*-tolylamine [5], was allowed to react with thallium cyclopentadienide in benzene, and then treated with TlOH. A stable gray powder was obtained and purified by sublimation at ca. 80°C under vacuum to give a yellow solid of the imidoyl-substituted cyclopentadienide salt I. Although NMR measurement of I was not carried out owing to its low solubility, the mass spectrum observed at ca. 80°C exhibited a well-defined parent-ion peak at *m/e* 429 (for ^{205}Tl) in accordance with the proposed structure. The IR spectrum showed a band for ν(C=N) at 1580 cm^{-1}.

The salt I was treated with chloro-bridged palladium(II) complexes, $[\{PdCl_2(PREt_2)\}_2]$ (R = Ph, Et), in THF at ca. 20°C to afford new palladium(II) complexes, $[Pd\{\eta^5\text{-}C_5H_4C(=NC_6H_4CH_3)CH(CH_3)_2\}Cl(PREt_2)]$ (II, R = Ph; III, R = Et), with the imidoyl-substituted cyclopentadienyl group. In addition, sodium salts of acetyl- and methoxycarbonylcyclopentadienyl groups reacted similarly at ca. -5°C to give their new palladium(II) complexes $[Pd(\eta^5\text{-}C_5H_4\text{-}COY)Cl(PPhEt_2)]$ (IV, Y = CH_3; V, Y = OCH_3). Complexes II and III were very stable, whereas complexes IV and V were slightly air-sensitive in common organic solvents. Tables 1–3 summarize the yields, analytical data, and some physical and spectroscopic properties of these new compounds (I–V) together with $[Pd(\eta^5\text{-}C_5H_5)Cl(PPhEt_2)]$ (VI), which was prepared for comparison.

TABLE 1

SYNTHESES AND PROPERTIES OF THE CYCLOPENTADIENYL COMPOUNDS

Compound	Yield (%)	M.p. [a] (°C)	Analyses (Found (calcd.) (%))			ν(C=N) [b] ν(C=O) (cm^{-1})	M^+ [c]
			C	H	N		
I	87	192–193	45.16	4.28	3.17	1580	429
			(44.83)	(4.23)	(3.27)		
II	65	160	58.58	6.41	2.29	1560	531
			(58.66)	(6.25)	(2.63)		
III	62	122–124	54.00	6.91	2.62	1558	483
			(54.56)	(6.87)	(2.89)		
IV	50	oil		[d]		1648	414
V	56	oil		[d]		1702	430
VI	43	87	48.06	5.39	0.00	–	372
			(48.28)	(5.40)	(0.00)		

[a] With decomposition in an evacuated capillary tube. [b] In KBr disk for I, II, and III; in dichloromethane for IV and V. [c] The strongest peak in the parent-ion isotope pattern of the mass spectrum. [d] Elemental analyses were not performed for these unstable compounds.

Comparatively strong ν(C=N) bands were observed near 1560 cm^{-1} in the IR spectra of II and III, and they were shifted from that of I towards lower wave-numbers by ca. 20 cm^{-1}. Complexes IV and V showed ν(C=O) bands at 1648 and 1702 cm^{-1}, respectively.

In each of the ^{1}H NMR spectra of II–V, four protons of the monosubstituted cyclopentadienyl groups appeared as two signals of equal intensity (2H). The signal at lower field was assigned to 2-H and 5-H neighboring the electron-withdrawing substituents, and the high-field signal was assigned to 3-H and 4-H. Analogous assignments have been made unequivocally for the monosubstituted cyclopentadienyl groups in [Fe(η^5-C_5H_5)(η^5-C_5H_4X)] [6], [Cr(η^5-C_5H_4X)$(CO)_2$(NO)] [7], [Rh(η^5-C_5H_4X)(1,4-diene)] [8], and [M(η^5-C_5H_4X)(CH_3)$(CO)_3$] (M = Cr, Mo, W) [9].

Three ^{13}C NMR signals were observed for the monosubstituted cyclopentadienyl

TABLE 2

SELECTED ^{1}H NMR DATA FOR THE CYCLOPENTADIENYLPALLADIUM(II) COMPLEXES [a]

Compound	C_5H_4 group		Y in $C_5H_4C(=X)Y$ (X = NR′ or O)		R′(*p*-tolyl group)		
	2-H 5-H	3-H 4-H	C*H*$_3$	C*H*(CH$_3$)$_2$	C*H*$_3$	2-H 6-H	3-H 5-H
II	6.23(bs)	5.92(bs)	1.23(d) [e]	2.92(sept) [e]	2.37(s)	7.23(d) [f]	6.98(d) [f]
III	6.82(bs)	6.03(bs)	1.25(d) [e]	2.93(sept) [e]	2.33(s)	7.15(d) [f]	6.88(d) [f]
IV [b]	6.07(m)	5.95(dd) [d]	2.25(s)				
V [b]	6.04(m)	5.88(dd) [d]	3.66(s)				
VI	5.65(d) [c]						

[a] δ Value (ppm) from TMS; in CD_2Cl_2. Abbreviations used: s, singlet; bs, broad singlet; d, doublet; dd, doublet of doublets; sept, septet; m, multiplet. Satisfactory spectral data were obtained for the tertiary phosphine moieties, but these data are omitted in this table. [b] Measured in a deoxygenated solution. [c] A signal for all ring-protons; *J* 2.5 Hz. [d] *J* 4.5 and 2.0 Hz. [e] *J* 7.0 Hz. [f] *J* 8.0 Hz.

TABLE 3

^{13}C NMR DATA FOR THE CYCLOPENTADIENYLPALLADIUM(II) COMPLEXES [a]

Compound	Cyclopentadienyl ring			$C_5H_4C(=X)Y$ (X = NR′ or O)	Y in $C_5H_4C(=X)Y$		R′(*p*-tolyl group)				
	1-C	(2-C, 5-C) (3-C, 4-C)			CH_3	$CH(CH_3)_2$	CH_3	1-C	2-C 6-C	3-C 5-C	4-C
II	148.7	135.7	91.2	183.3	21.5	32.3	21.1	144.1	124.1	129.1	135.5
III	148.7	135.5	90.5	183.2	21.5	32.4	21.1	144.1	124.1	129.0	135.5
IV [b]	121.5	103.7	99.9(d) [c]	189.3	36.5	–	–	–	–	–	–
VI		100.3(d) [d]		–	–	–	–	–	–	–	–

[a] δ Value (ppm) from TMS; in CD_2Cl_2. The shape of the signal was a singlet, unless stated otherwise; d, doublet due to coupling with ^{31}P. Satisfactory spectral data were obtained for the tertiary phosphine moieties, but these data are omitted in this table. [b] Measured in a deoxygenated solution. [c] *J* 6.1 Hz. [d] A signal for all ring-carbons; *J* 2.4 Hz.

groups in II–IV, as listed in Table 3. In comparison with the cases of VI and the monosubstituted cyclopentadienyl complexes reported so far [10], the groups in II and III gave two resonances at considerably lower fields. The signal at the lowest field of the three had a relatively low intensity, and was readily attributed to the quaternary carbon 1-C with the aid of the off-resonance technique. However, it was not possible at this stage to assign the remaining two resonances to the couple of 2-C and 5-C and that of 3-C and 4-C, without an intensive study using selective proton decoupling.

The palladium(II) complexes II–VI exhibited characteristic fragmentation in their mass spectra, and there were [Pd(η^5-cyclopentadienyl)Cl(tertiary phosphine)]$^+$, [PdCl(tertiary phosphine)]$^+$, and [Pd(tertiary phosphine)]$^+$ fragment ions. Furthermore, complexes II and III gave interesting fragments, $[Pd\{\eta^5\text{-}C_5H_4C(=NC_6H_4CH_3)CH(CH_3)_2\}(PREt_2)]^+$ (R = Ph, Et), resulting from loss of chlorine from their parent ions, but other complexes did not. The strong π-bonding between the cyclopentadienyl group and palladium in II and III may be related to the extended delocalized π-system of the complexed cyclopentadienyl ring towards the imidoyl substituent. The delocalization was confirmed by the aforementioned shifts of the ν(C=N) bands. In addition, the noticeable stability of II and III and the difference in color * between these two and complexes IV–VI are probably associated with the extended delocalization.

Experimental

General procedures

Melting points were determined in evacuated capillary tubes on a Yanagimoto Mp-S3 microstage apparatus and are uncorrected. IR spectra were recorded on a Hitachi model 285 spectrometer. ^{1}H NMR spectra were run on a Japan Electron Optics Laboratory (JEOL) model JNM-MH-100 spectrometer, using tetramethylsilane as the internal standard. ^{13}C NMR spectra were measured on a JEOL FX-90-Q spectrometer. Mass spectra were obtained with a Nichiden-Varian TE-600 gas chromatograph-mass spectrometer. Sodium acetylcyclopentadienide [11], sodium methoxycarbonylcyclopentadienide [11], imidoyl chloride [5], and chloro-bridged dinuclear palladium(II) complexes $[\{PdCl_2(PREt_2)\}_2]$ [12] were prepared according to literature methods.

Thallium salt of the imidoyl-substituted cyclopentadienyl group

N-1-(2-Methyl-1-chloropropylidene)-*p*-tolylamine (1.56 g) in benzene was added slowly to a benzene suspension of thallium cyclopentadienide (2.16 g) at a temperature below 10°C and the mixture was stirred for 1 h. After warming to ca. 25°C and additional stirring for 5 h, the mixture was filtered. The filtrate was treated with TlOH (ca. 2 g) in benzene and stirred for 15 h. The collected precipitates were washed with benzene, methanol, and ether to give the thallium salt $Tl[C_5H_4C(=NC_6H_4CH_3)CH(CH_3)_2]$ (I) (3.0 g). An analytical sample was obtained as yellow microcrystals by sublimation at ca. 80°C.

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* UV and VIS spectral data (CH_2Cl_2): II, 229 (ϵ 20740), 279 (20990), ca. 325 (sh, 8500), and ca. 380 nm (sh, 4500); VI, 240 (ϵ 19140), 295 (10530), 371 (5120), and 606 nm (88).

Palladium(II) complexes of the imidoyl-substituted cyclopentadienyl group

The complex [{$PdCl_2(PPhEt_2)$}$_2$] (0.42 g) was added to a THF suspension of I (0.52 g) and the mixture was stirred for 4 h. After thallium chloride had been removed by centrifugation, the supernatant solution was concentrated and passed through a silica-gel column. An orange fraction was obtained on elution with benzene/dichloromethane (5/1) and the solution was concentrated. Addition of ether gave a yellow powder of the complex [Pd{η^5-$C_5H_4C(=NC_6H_4CH_3)CH(CH_3)_2$}$Cl(PPhEt_2)$] (II) (0.42 g). Similar reaction of I with [{$PdCl_2(PEt_3)$}$_2$] yielded a yellow powder of [Pd{η^5-$C_5H_4C(=NC_6H_4CH_3)CH(CH_3)_2$}$Cl(PEt_3)$] (III).

Palladium(II) complexes with the acetyl- and methoxycarbonylcyclopentadienyl groups

Sodium acetylcyclopentadienide (0.13 g) was dissolved in THF under dry nitrogen and cooled to −5°C. The complex [{$PdCl_2(PPhEt_2)$}$_2$] (0.40 g) was added in portions and the mixture was stirred for 30 min. After centrifugal separation, the supernatant solution was concentrated and chromatographed on a silica-gel column. A deep green fraction was collected by elution with dichloromethane/ether (5/1) and it afforded a deep green oil of [$Pd(\eta^5$-C_5H_4-$COCH_3)Cl(PPhEt_2)$] (IV) (0.24 g). Using a similar preparative method of IV, the complex [$Pd(\eta^5$-$C_5H_4COOCH_3)Cl(PPhEt_2)$] (V) was obtained as a deep green oil.

The cyclopentadienyl palladium(II) complex [$Pd(\eta^5$-$C_5H_5)Cl(PPhEt_2)$] (VI)

This was prepared as a deep green powder by treating thallium cyclopentadienide with [{$PdCl_2(PPhEt_2)$}$_2$], using a method similar to that of [$Pd(\eta^5$-$C_5H_5)Cl(PEt_3)$] reported by Cross and Wardle [13].

References

1 (a) R.V. Parish and M.I. Vania, J. Organomet. Chem., 260 (1984) 41; (b) T. Hayashi, N. Nagashima and M. Kumada, Tetrahedron Lett., 21 (1980) 4623; (c) A.J. Naaktgeboren, R.J.M. Nolte and W. Drenth, J. Am. Chem. Soc., 102 (1980) 3350; (d) A. Sekiya and J.K. Stille, J. Am. Chem. Soc., 103 (1981) 5096.
2 (a) J.P. Farr, M.M. Olmstead, C.H. Hunt and A.L. Balch, Inorg. Chem., 20 (1981) 1182; (b) D.A. Wrobleski and T.B. Rauchfuss, J. Am. Chem. Soc., 104 (1982) 2314; (c) N.E. Schore, L.S. Benner and B.E. Labelle, Inorg. Chem., 20 (1981) 3200.
3 (a) V.I. Sokolov, L.L. Troitskaya and O.A. Reutov, J. Organomet. Chem., 133 (1977) C28; (b) 182 (1979) 537.
4 (a) D.W. Macomber, W.P. Hart and M.D. Rausch, Adv. Organomet. Chem., 21 (1982) 1 and ref. cited therein; (b) D.W. Macomber, W.P. Hart and M.D. Rausch, J. Am. Chem. Soc., 104 (1982) 884; (c) M.D. Rausch, B.H. Edwards, R.D. Rogers and J.L. Atwood, ibid., 105 (1983) 3882.
5 H. Ulrich, The Chemistry of Imidoyl Halides, Plenum Press, New York, 1968.
6 M.D. Rausch and A. Siegel, J. Organomet. Chem., 17 (1969) 117.
7 M.D. Rausch, E.A. Mintz and D.W. Macomber, J. Org. Chem., 45 (1980) 689.
8 M. Arthurs, S.M. Nelson and M.G.B. Drew, J. Chem. Soc., Dalton Trans., (1977) 779.
9 D.W. Macomber and M.D. Rausch, J. Organomet. Chem., 258 (1983) 331.
10 B.E. Mann and B.F. Taylor, ^{13}C NMR Data for Organometallic Compounds, Academic Press, New York, 1981.
11 W.P. Hart, D.W. Macomber and M.D. Rausch, J. Am. Chem. Soc., 102 (1980) 1196.
12 J. Chatt and L.M. Venanzi, J. Chem. Soc. A, (1957) 2351.
13 R.J. Cross and R. Wardle, J. Chem. Soc. A, (1971) 2000.