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RHODIUM(II)2,4,6-TRIARYLBENZOATES : IMPROVED CATALYSTS FOR THE SYN CYCLOPROPANATION OF Z-OLEFINS

H.J. CALLOT* and F. METZ

L.A.n°31, Institut de Chimie, Université Louis Pasteur, 1 rue Blaise Pascal, 67008 Strasbourg, France

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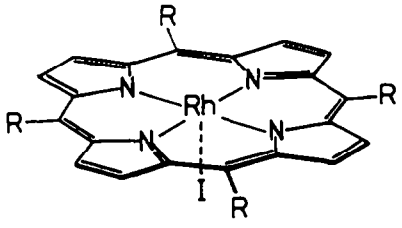
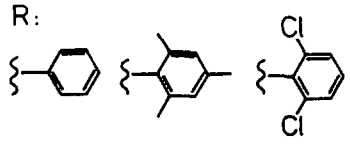
Abstract - The stereochemical course of the cyclopropanation of Z-olefins by ethyl diazoacetate in the presence of various binuclear rhodium(II)carboxylates was studied. The highest syn/anti ratio (up to > 3) was obtained using $Rh_2(O_2CR)_3(O_2CR')$ where R = 2,4,6-triarylphenyl and R' = CH_3 or CF_3.

In a preceding article[1] we described the effect of rhodium(III)porphyrins 1, 2, 3 [2] as catalysts for the cyclopropanation of Z-olefins with ethyl diazoacetate (EDA) : a large increase in syn ester formation was observed, contrasting with the effect of all other catalysts which favor the anti isomer. We attributed the change in product distribution to the large steric hindrance introduced by the meso-aryl substituents. Attempts to increase the size of these meso substituents proved to be unsuccessful, both the ligand synthesis and the introduction of rhodium beeing exceedingly sensitive to steric hindrance. We thus turned our attention to a class of very active and widely used cyclopropanation catalysts, the binuclear rhodium(II)carboxylates[3,4]. In this article we will describe the synthesis and use of selected carboxylate ligands which led to a large improvement of the syn/anti selectivity (see fig. page 3).

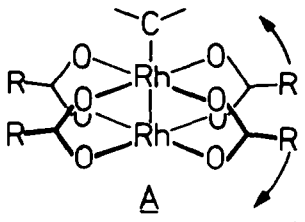




1 2 3

1. Symetrical rhodium(II)carboxylates $Rh_2(O_2CR)_4$

If one postulates an intermediate (rhodium carboxylate)-carbene complex of type A any R group that will extend in the directions indicated by arrows should show a better syn/anti selectivity than, for example, the corresponding acetate (R = CH_3). This has been demonstrated for the pivalate 4 (R = t-Bu)[4], although to a low extent (reaction with cyclohexene) and the concept utilized to modify the regioselectivity of the carbethoxycarbene insertion into C-H bonds of paraffins[3b]. Following this line we synthesized compounds 5-9 from $Rh_2(O_2CCH_3)_4$ by exchange[5] with the corresponding acid while codistilling CH_3COOH with chlorobenzene.



A

$$Rh_2(O_2CCH_3)_4 \xrightarrow[\text{dist. } C_6H_5Cl]{RCOOH} Rh_2(O_2CR)_4$$

R = $-C(C_6H_5)_3$ 5 (77 %) ; - dehydroabietyl 6 (52 %) ; 1-adamantyl 7 (48 %) ; -9-anthracenyl 8 (26 %) ; -mesityl 9 (29 %).

Cyclopropanation of cyclohexene showed a substantial difference with 4 only for ortho-disubstituted R groups (8 and 9), but the figure was still below that measured for 2 or 3 (see Table I). None of these catalysts showed a drop in activity up to a 10^3 turnover.

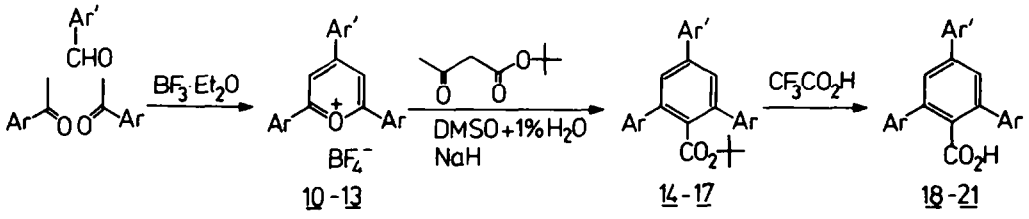
Table I

Catalyst	syn % *	anti % *	allylic insertion % *	syn/anti ratio
4	27	71	2	0.38
5	25	71	4	0.35
6	25	71	4	0.35
7	31	66	3	0.47
8	34	59	7	0.57
9	40	57	3	0.70
2	50	42	8	1.2

* Relative yields (small scale experiments, turnover = 10^3).

2. Synthesis of rhodium(II)triarylbenzoates

To increase the size and rigidity of the ortho groups we decided to replace the methyl groups in 9 by aryl substituents. While o,o'-diarylbenzoic acids were not easily available, the access to a series of 2,4,6-triarylbenzoic acids was made easier by improving the literature [6] reaction conditions and yields (NaH, "wet" DMSO, 20°C instead of t-BuOK/t-BuOH, 1 h reflux ; t-butyl acetoacetate to allow an easy deprotection of the carboxy group by trifluoroacetic acid instead of refluxing 30 % methanolic KOH to cleave the ethyl ester ; 24 % → ca 30-70 % ; reaction sequence below).



As in the above examples displacement of acetic acid by the triarylbenzoic acids transformed $Rh_2(O_2CCH_3)_4$ into the benzoates 22-29. However the reaction proceeded slowly and we obtained a mixture of esters which could be separated by silicagel chromatography. In particular the yield of the fully exchanged rhodium complex (x = 4 ; y = 0) decreased with the size of the Ar group and it could not be detected when Ar = p-t-butylphenyl. Similarly, but starting with rhodium(II) pivalate and trifluoroacetate, we obtained complexes 30 and 31 (table II).

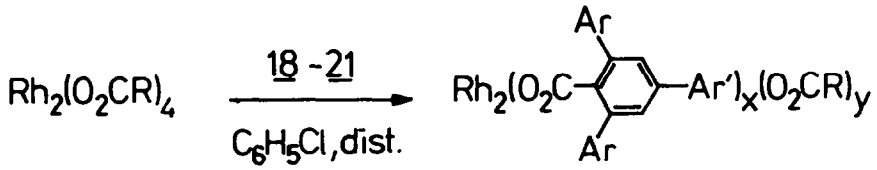


Table II

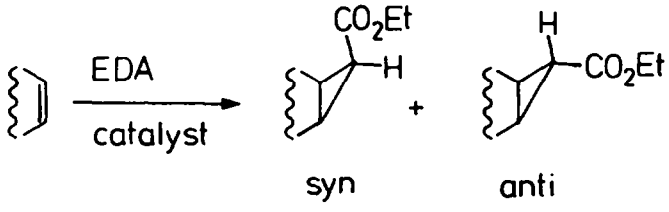
	Ar	Ar'	R	x	y	Yield % [a]
22	phenyl	phenyl	CH_3	3	1	16 [a]
23	phenyl	phenyl	CH_3	4	0	50
24	p-tolyl	p-tolyl	CH_3	3	1	11 [a]
25	p-tolyl	p-tolyl	CH_3	4	0	41
26	p-biphenyl	phenyl	CH_3	3	1	17 [a]
27	p-biphenyl	phenyl	CH_3	4	0	4
28	p-t-Bu-phenyl	phenyl	CH_3	2	2	60 [b]
29	p-t-Bu-phenyl	phenyl	CH_3	3	1	17
30	p-tolyl	p-tolyl	t-Bu	3	1	25 [a]
31	p-tolyl	p-tolyl	CF_3	3	1	29

[a] The esters (x = y = 2) and a small amount of a polymeric material were present, but were not characterized.

[b] Same comment but x = 1, y = 3.

3. Catalytic activity of rhodium(II)triarylbenzoates

The reactions (general scheme below) were run under our standard procedure : very slow addition (automatic syringe) of an EDA/olefin mixture to the olefin + catalyst solution heated at 60°C. The olefin/EDA and EDA/catalyst ratios were kept at 7.5-10 and 1500-2000 respectively. The composition of the resulting mixture was analyzed (GC) and the yields measured after silicagel chromatography. In the case of cyclohexene, a small amount of allylic insertion product was always detected.



Complexes 23, 25 and 27 (x = 4) did not catalyze the cyclopropanation reaction and their destruction was illustrated by a rapid color change from green to yellow and the absence of N_2 evolution.

On the contrary 22, 24, 26 and 29-31 are very active catalysts, at least up to a ca 10^3 turnover. However at higher turnover values the color became yellow with concomitant slowing of the N_2 evolution.

As with catalysts 5-9 no deactivation was observed for 28 (x = 2) the color and rate of N_2 evolution being constant over the whole reaction period.

4. Product distribution. Syn/anti selectivity (rhodium(II)triarylbenzoates)

Three representative olefins were submitted to the cyclopropanation conditions : cyclohexene, norbornene, 1-hexene. In the case of cyclohexene, the reaction was monitored by sampling the mixture at various turnover values and analyzing (GC) the esters to estimate the influence of the catalyst transformation on the syn/anti ratio. These measurements allowed us to extrapolate the syn/anti ratio at t = 0 and evaluate the selectivity of the intact catalyst. Table III gives the syn/anti ratios at a 10^3 turnover (DAE/catalyst = 10^3) and extrapolated syn/anti ratios for cyclohexene.

Table III

Catalyst	Olefin	% syn [a]	% anti [a]	syn/anti	extrapolated syn/anti ratio t = 0	monoesters total yield % [b]
22	Cyclohexene	67	33	2.0	2.2	78
24	"	72	28	2.6	3.6	80
26	"	74	26	2.8	3.8	68
29	"	73	27	2.7	3.9	71
30	"	58	42	1.4	1.7	77
31	"	72	28	2.6	4.5	52
28	"	30	70	0.43	0.43	[c]
22	1-hexene	63	37	1.7	-	59
24	"	66	34	1.9	-	83
26	"	67	33	2.0	-	89
2	"	47	53	0.9	-	85
22	norbornene	69	31	2.2	-	39
24	"	55	45	1.2	-	9
2	"	68	32	2.1	-	76

[a] Relative yields (turnover = 10^3) ± 1 %

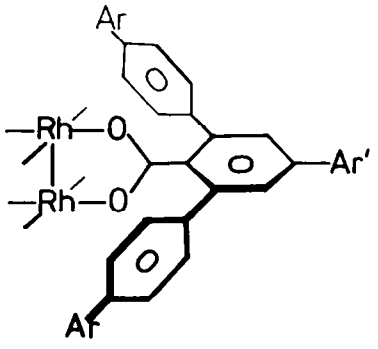
[b] Including, when cyclohexene is used as substrate, the allylic insertion product [ethyl(cyclohex-2-ene)-1-yl-acetate] which amount for 5-10 % depending on the catalyst.

[c] Small scale experiment.

DISCUSSION

The case of catalysts 5-9 is clear : none of the R groups is large enough to substantially improve the selectivity (see data for 2 in table I). On the contrary, depending on the degree of substitution (n = 2, 3, 4) the triarylbenzoates show an extremely large reactivity/stability/selectivity variation : no reactivity and low stability (x = 4), high reactivity and selectivity but moderate stability (x = 3), high reactivity and stability but low selectivity (x = 2).

To interpret these results one must be able to appreciate the geometry of the triarylbenzoate group, especially in the vicinity of the catalytic site. Three biphenyl-type interactions between phenyls or between the Rh_2O_2C cycle and the central phenyl will force the triarylbenzoate group to wrap around the $Rh_2O_8C_4$ skeleton like a helix-fragment (scheme below). The crystal structure of rhodium(II)orthophenylbenzoate show the outline of this phenomenon [7]. If n = 2 and if the two esters are in trans situation a rotation across the C_1-C_2 bond may still be possible. However two vicinal triarylbenzoates (x > 2) will block each other as was demonstrated by space-filling models. The ortho-aryl group will project obliquely above the RhO_4 plane and form a wall interrupted by a loophole corresponding to the remaining acetate, if any.



When x = 4 an access to the metal along the Rh-Rh axis is still possible (as was demonstrated by the formation of a pyridine complex) but any ligand (including an intermediate carbene)will act as a plug. A second molecule, like an olefin or another EDA, will no more be able to approach the metal center and self decomposition of the material will be the prefered pathway.

The presence of a smaller ligand (catalysts 22, 24, 26, 29-31 ; x = 3) permits this approach and the reaction may proceed catalytically. The syn/anti selectivity is clearly a function of steric hindrance the largest increase occurring on substitution of the ortho-phenyl groups, the differences between CH_3, C_6H_5 or t-Bu (24, 26, 29) being of low significance. An increase of the size of the "small" ester (CH_3 → t-Bu, 24 → 30) will "symetrize" the catalytic site and thus diminish the selectivity but not the activity. A slight effect was observed when replacing acetate by trifluoroacetate.

At the other end of the scale catalyst 28, which probably possesses two trans-triarylbenzoate groups show a very low selectivity, almost as low as $Rh_2(O_2C$t-Bu$)_4$. The two independent large esters leave the catalytic site wide open and interfer to a very limited extend with the course of the reaction.

The comments apply well to the case of cyclohexene and 1-hexene, but not to norbornene. Although the drop in selectivity is not easy to explain it is obvious from the yield drop that severe interactions between the reactants and the ester ligands occur during the reaction.

A last point deserves some comments : why did we observe a slow deactivation of the catalysts (x = 3) and a drop of the syn/anti ratio ? We think that the large steric compression introduced may play a role. Any process that will reduce this compression by releasing an ester ligand will be favored. We did not investigate the "deactivated" products but from the selectivity data we think that some of them might still show catalytic activity but with a very low syn/anti ratio. One should also notethat rhodium tris-triarylbenzoates do not catalyze the insertion of carbene into C-H bonds of n-alkanes (deactivation takes place before any substantial reaction could be detected) although hindered catalysts like rhodium(III)porphyrins [2] and selected hindered rhodium(II)carboxylates [3b] are active under similar conditions.

EXPERIMENTAL SECTION

N.m.r. spectra were recorded on Perkin-Elmer R-12 (60 MHz) and Bruker WP-200 SY (200 MHz) spectrometers. The chemical shifts are expressed in ppm (TMS δ = 0) and the coupling constants in Hz. Combustion analyses were performed by the Service de Microanalyse de l'Institut de Chimie de Strasbourg. Gas chromatographic analyses were carried out using a Perkin-Elmer Sigma 3B chromatograph equipped with a CP Sil 19 CB capillary column (length 10 m, diameter 0.23 mm).

$Rh_2(O_2CCH_3)_4$ and $Rh_2(O_2C$t-Bu$)_4$ were prepared according to ref. 8.

The analytical figures for acid 21 and catalyst 23 could not be improved (4 attempts ; best data given below).

Catalysts 5-9

A mixture of $Rh_2(O_2CCH_3)_4$ (50 mg ; 0.113 mM), the corresponding acid (5-10 eq.) and chlorobenzene (20 mL) was heated to reflux and the solvent slowly distilled. The course of the reaction was followed by t.l.c. After consumption of the starting material the solvent was evaporated and the residue taken up in CH_2Cl_2 and chromatographed (alumina, 20 g, eluent CH_2Cl_2 + AcOEt 70:30). The blue band was collected and the product crystallized from CH_2Cl_2/MeOH (5-9 incorporated two molecules of H_2O per molecule in the crystal).

5 (77 %) Anal. Calcd for $C_{40}H_{60}O_8Rh_2.2H_2O$: C, 69.06 ; H, 4.64. Found : C, 68.5 ; H, 4.5. N.m.r. ($CDCl_3$) : 6.4-7.1 (m, phenyl).

6 (52 %) Anal. Calcd for $C_{80}H_{108}O_8Rh_2.2H_2O$: C, 66.75 ; H, 7.84. Found : C, 66.2 ; H, 7.8. N.m.r. ($CDCl_3$) : 0.9-3.0 (m, 27H, diterpenic fragment - phenyl), 6.7-7.3 (m, 3H, phenyl).

7 (48 %) This product was already described. See ref. 7.

8 (26 %) Anal. Calcd for $C_{60}H_{36}O_8Rh_2.2H_2O$: C, 63.95 ; H, 3.57. Found : C, 63.4 ; H, 3.4. N.m.r. ($CDCl_3$) : 6-8.4 (m, anthracenyl).

9 (29 %) Anal. Calcd for $C_{40}H_{44}O_8Rh_2.2H_2O$: C, 53.70 ; H, 5.40. Found : C, 53.5 ; H, 5.5. N.m.r. ($CDCl_3$) : 2.1 (s, 24H, ortho CH_3), 2.2 (s, 12H, para CH_3), 6.7 (s, 8H, phenyl).

Pyrylium salts 10-13

We used the general method described by Lombard and Stephan [9] to prepare 10-13 (salts 10-12 were described in ref. 9).

Salt 13 : A mixture of p-t-butylacetophenone (2.75 g ; 15.6 mM) and benzaldehyde (0.83 g ; 7.83 mM) in $BF_3.Et_2O$ (2.4 mL, 16.8 mM) was heated to 100°C for 10 mn. After cooling the salt was precipitated by addition of cyclohexane, filtered and washed several times with Et_2O/cyclohexane 3:7. Yellow crystals (0.85 g ; 22 %). Mp 258-260° (dec.). Anal. Calcd for $C_{31}H_{33}OBF_4$: C, 73.24 ; H, 6.54. Found : C, 73.3 ; H, 6.7. N.m.r. (CD_3CN) : 1.45 (s, 18H, t-butyl), 7.5-7.9 (m, 7H, m+p phenyl), 8.1-8.3 (m, 6H, o-phenyl), 8.55 (s, 2H, pyrylium).

t-Butyl triarylbenzoates 14-17

The procedure described by Dimroth and Neubahr [6] was modified as follows. A suspension of NaH (50 % in oil ; 480 mg ; 10 mM) in wet DMSO (1 % H_2O ; 20 ml) was heated to 60°C and stirred under argon until a clear solution resulted. It was cooled to 20°C and t-butylacetoacetate (0.82 mL ; 5.02 mM) followed by the pyrylium salt (5.05 mM) were added. The mixture turned immediatly purple and slowly discolored. After 0.5 h it was diluted with toluene (50 mL), washed (H_2O ; 3x20 mL). The aqueous phase was extracted with toluene (2x15 mL). The total organic solution was washed again (H_2O ; 7x20 mL) and dried (Na_2SO_4). After evaporation the residue was chromatographed (silicagel ; 100 g ; toluene). At this stage esters 16 and 17 were obtained pure, while an impurity is still present in 14 and 15. All esters were used as such for the next step.

Triarylbenzoic acids 18-21

The ester fraction from last step was dissolved in CH_2Cl_2 (10 mL) and CF_3COOH (10 mL). After 3 h (14 and 15), 15 h (16) or 7 h (17) t.l.c. indicated the completion of the protolysis. After evaporation the residue was chromatographed (silicagel ; 100 g ; eluent : CH_2Cl_2/AcOEt, gradient from 80:20 to 65:35 to purify 18 and 19, 90:10 for 20) or directly crystallized (21). Acids 20 and 21 seem to crystallize with ca 1.5 and 1 molecules of water which could not be eliminated on prolonged pumping.

Acid 18 [6] (67 % from the pyrylium salt 10).

Acid 19 (32 % from 11 ; crystallized from CH_2Cl_2/hexane). Mp 207-208°C. N.m.r. ($CDCl_3$) : 2.40 (s, 9H, CH_3), 7.0-7.65 (m, 14H, phenyl). Anal. Calcd for $C_{28}H_{24}O_2$: C, 85.68 ; H, 6.16. Found : C, 85.5 ; H, 6.3.

Acid 20 (43 % from 12 ; crystallized from CH_2Cl_2/MeOH). Mp 215-217°C. N.m.r. ($CDCl_3$) : 7.15-7.8 (m, phenyl). Anal. Calcd for $C_{37}H_{26}O_2.1.5H_2O$: C, 83.91 ; H, 5.52. Found : C, 84.2 ; H, 5.7.

Acid 21 (49 % from 13 ; crystallized from CH_2Cl_2/MeOH). Mp 233-235°C. N.m.r. ($CDCl_3$) : 1.45 (s, 18H, t-butyl), 7.35-7.7 (m, 15H, phenyl). Anal. Calcd for $C_{33}H_{34}O_2.H_2O$: C, 82.46 ; H, 7.55. Found : C, 83.3 ; H, 7.9.

Catalysts 22-31

General procedure from $Rh_2(O_2CCH_3)_4$: To a suspension of finely divided $Rh_2(O_2CCH_3)_4$ (50 mg ; 0.113 mM) in chlorobenzene was added the triarylbenzoic acid (0.452 mM). The mixture was heated to reflux and chlorobenzene was distilled. The level of the liquid was maintained constant by simultaneous slow addition of chlorobenzene from a dropping funnel. The reaction course was followed by t.l.c. (silicagel ; CCl_4/CH_2Cl_2 3:1). After distillation of ca 350 ml chlorobenzene and evaporation (vacuum) the residue was dissolved in CCl_4/CH_2Cl_2 3:1 (2 ml) and chromatographed (silicagel ; 30 g ; same eluent). Complexes 23, 25 and 27 (x = 4) were eluted first followed by 22, 24 and 26. Similarly 29 eluted more rapidly than 28. All compounds were crystallized from CH_2Cl_2/MeOH and pumped (10^{-2}Torr) overnight. They incorporate at least 2 (up to 4) molecules of water per molecule of rhodium complex.

The preparation of 30 and 31 followed the same procedure but starting with $Rh_2(O_2C\text{-}t\text{-}Bu)_4$ or $Rh_2(O_2CCF_3)_4$.

22 (16 %) N.m.r. ($CDCl_3$) : 1.55 (s, 3H, CH_3), 6.8-7.7 (m, 51H, phenyl). Anal. Calcd for $C_{77}H_{54}O_8Rh_2.2H_2O$: C, 68.55 ; H, 4.33. Found : C, 69.1 ; H, 4.3.

23 (50 %) N.m.r. ($CDCl_3$) : 6.8-7.75 (m, phenyl). Anal. Calcd for $C_{100}H_{68}O_8Rh_2.2H_2O$: C, 73.26 ; H, 4.43. Found : C, 72.3 ; H, 4.4.

24 (11 %) N.m.r. ($CDCl_3$) : 1.75 (s, 3H, acetate), 2.30, 2.35 and 2.39 (3s, 27H, tolyl CH_3), 6.8-7.55 (m, 42H, phenyl). Anal. Calcd for $C_{86}H_{72}O_8Rh_2.2H_2O$: C, 70.01 ; H, 5.19. Found : C, 69.4 ; H, 5.3.

25 (41 %) N.m.r. ($CDCl_3$) : 2.25 (broad s, 36H, tolyl CH_3), 6.7-7.7 (m, 56H, phenyl). Anal. Calcd for $C_{112}H_{92}O_8Rh_2.2H_2O$: C, 74.41 ; H, 5.46. Found : C, 73.9 ; H, 5.6.

26 (17 %) N.m.r. ($CDCl_3$) : 1.68 (s, 3H, CH_3), 6.8-7.8 (m, 75H, phenyl). Anal. Calcd for $C_{115}H_{78}O_8Rh_2.4H_2O$: C, 74.08 ; H, 4.65. Found : C, 74.1 ; H, 4.7.

27 (4 %) N.m.r. ($CDCl_3$) : 6.7-7.8 (m, phenyl). Anal. Calcd for $C_{148}H_{100}O_8Rh_2.4H_2O$: C, 77.82 ; H, 4.77. Found : C, 77.7 ; H, 4.8.

28 (60 %) N.m.r. ($CDCl_3$) : 1.3 (s, 36H, t-butyl), 1.7 (s, 6H, acetate CH_3), 6.9-7.85 (m, 30H, phenyl). Anal. Calcd for $C_{70}H_{72}O_8Rh_2.3H_2O$: C, 64.61 ; H, 6.04. Found : C, 64.4 ; H, 6.0.

29 (17 %) N.m.r. ($CDCl_3$) : 1.21 and 1.25 (2s, 54H, t-butyl), 1.34 (s, 3H, acetate CH_3), 7.1-7.5 (m, 45H, phenyl). Anal. Calcd for $C_{101}H_{102}O_8Rh_2.2H_2O$: C, 71.96 ; H, 6.34. Found : C, 72.1 ; H, 6.2.

30 (25 %) N.m.r. ($CDCl_3$) : 0.9 (s, 9H, t-butyl), 2.3 and 2.5 (s, 27H, CH_3), 6.8-7.7 (m, 42H, phenyl). Anal. Calcd for $C_{89}H_{78}O_8Rh_2.2H_2O$: C, 70.44 ; H, 5.45. Found : C, 70.5 ; H, 5.5.

31 (29 %) N.m.r. ($CDCl_3$) : 2.22 and 2.30 (2s, 27H, tolyl CH_3), 6.7-7.5 (m, 42H, phenyl). Anal. Calcd for $C_{86}H_{69}F_3O_8Rh_2.2H_2O$: C, 67.54 ; H, 4.81. Found : C, 68.1 ; H, 5.0.

SPECTRAL MEASUREMENTS

To compare the accessibility of the apical sites $Rh_2(O_2C\text{-}t\text{-}Bu)_4$ and 23 were dissolved in CH_2Cl_2 and visible spectra run in the absence of added ligand (A) or in the presence of excess MeOH (B) or pyridine (C) :

	A	λ(ε)	B		C	
$Rh_2(O_2C\text{-}t\text{-}Bu)_4$	636	(177)	596	(160)	506	(268)
	426	(112)	440	(91)		
23	644	(180)	612	(185)	532	(268)
	448	(137)	460	(98)		

Olefins cyclopropanation

To a solution of catalyst (5 mg) in olefin (2 mL) kept at 60°C was slowly added a solution of EDA (0.6 mL) in olefin (4.4 mL) (automatic syringe ; 0.07 mL/min ; addition over 70 min). At intervals corresponding to the addition of 0.5, 1, 2.5 and 5 mL of the syringe solution a 2 µL sample of the reaction mixture was drawn, diluted with hexane and analyzed (GC). At the end of N_2 evolution, the excess olefin was evaporated and the residue chromatographed on silicagel (20 g ; eluent hexane/AcOEt 98:2). The purity of the monoester fraction was then checked (GC) and the yield calculated/EDA.

REFERENCES AND NOTES

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