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(KR)
(A)

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C07F 19/00

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(43)

2002 - 0005366
2002 01 17

(21)	10 - 2000 - 7013037
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(86)	1999 05 11

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(87)	1999 11 25

[illegible]

(30) 98/06558 1998 05 20 (FR)

(71)

- 69190 -

(72)

- 31320 1

- 48145 11

- 69280 26

- 31000 가 25

- 31400 3

- 69002 29

(74)

$$\vdots$$

(54)

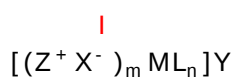
tionic) (dica

(dicationic)

EP - A - 0,798,041 5 -, 6 - 7 - EP - A - 0,721,953
8, 9 10
가

가 가 0

가



(:

- Z^+ - , 1,2,4 - - 5 -

- L ,

- M The Chemical Rubber Company " Handbook of Chemistry and Physics, 51 " (1970 - 1971)
1b, 2b, 3b, 4b, 5b, 6b, 7b, 8 ,

- X^- ,

- m 1 6 ,

- n 0 5 ,

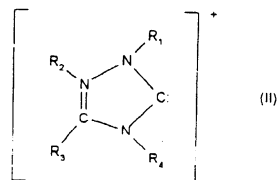
$$-m \quad n \quad 6 \quad ,$$

- Y 가).

Y I .

1,2,4 - - 5 - Z⁺ II :

11


$$[\quad , R_1, R_2, R_3 \quad R_4 \quad , \quad :]$$

— ,

- COOM₁, - SO₃ M₁, - PO₃ M₁ (, M₁ , ,
- N(R)₄ (, R , 1 4
) ,)

$$-N(R)_3 Y_a(\quad, R \quad, \quad, \quad), \quad 1 \quad 12$$

- OH,

- COOM₁, - SO₃ M₁, - PO₃ M₁ (, M₁ , ,
- N(R)₄ (, R , 1 12
)),

$$-N(R)_3 Y_a(\quad, R \quad, \quad, \quad, \quad), \quad 1 \quad 12$$

- OH,

 R_3

$R_1 \quad / \quad R_4 \quad , \quad 1,2,4 - \quad - 5 - \quad M$

L

(bidentate)

R₁ / R₄

(tridentate)

1,2,4 -

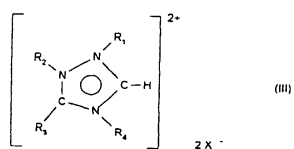
- 5 -

M

0, .

X⁻ , M
1,2,4 - -5 -

III



($\quad$,
- $R_1, R_2, R_3 \quad R_4$ II 1,2,4 - - 5 - 가 ,
- X^- I).

$$R_1, R_3, R_4 \text{ III } XR_2 (\quad, X \quad R_2 \quad \text{가} \quad)$$

[T.J. Curphey K.S. Prasad, Journal of Org. Chem., 1972, 37, 2259]

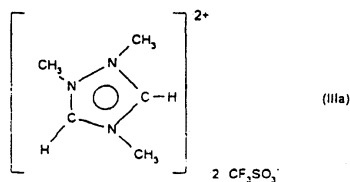
I
가
III
M
M
III
25
150
X -
(NMR)

I
III
(DMSO),
(DMSO)
가
2 -
(Heck)
가,

(III)

1. (IIIa) :

IIIa



[J. Org. Chem., 1972, 37, p. 2259]

1H - 1,2,4 - 2 (2 4)

1,2 - (IIIa)

160 - 162

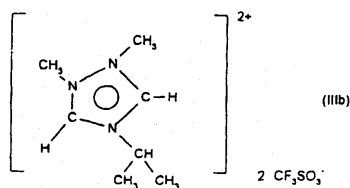
:

- ^1H NMR (d_6 -DMSO): δ 4.22 (s, 3H, CH_3N), 4.50 (s, 6H, CH_3N), 10.79 (s, 2H, H 사이클).

- ^{13}C NMR (H) (CD_3CN): δ 38.67 (s, CH_3N), 38.87 (s, $2\text{CH}_3\text{N}$), 120.35 (q, $^1J_{\text{CF}} = 320.1$ Hz, CF_3), 147.72 (s, 2C 사이클).

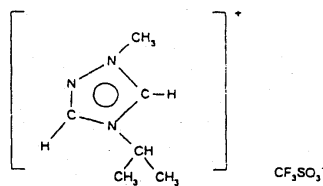
2. (IIIb) :

IIIb



가, 1H-1,2,4- (3) 1,2-) 4 (R₄)

:



91 %

가 24 (22 mmol) 2.5 ml 1,2- 20 ml 5 g (18 mmol)
1,2-

(IIIb) 163 - 165 73 %

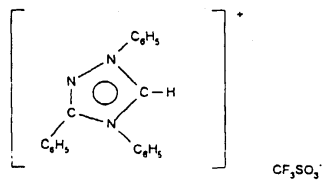
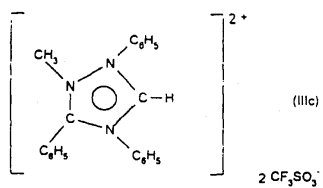
:

- ^1H NMR (CD_3CN): δ 1.65 (d, $^3J_{\text{HH}} = 6.58$ Hz, 6H, CH_3CH), 4.34 (s, 3H, CH_3N), 5.03 (sept, $^3J_{\text{HH}} = 6.58$ Hz, 1H, $[\text{CH}_3]_2\text{CHN}$), 10.22 (s, 2H, H 사이클).

- ^{13}C NMR (CD_3CN): δ 21.51 (s, CH_3CH), 38.71 (s, CH_3N), 58.88 (s, $[\text{CH}_3]_2\text{CHN}$), 120.35 (q, $^1J_{\text{CF}} = 320.1$ Hz, CF_3), 145.22 (s, 2C 사이클).

3. (IIIc) :

IIIc



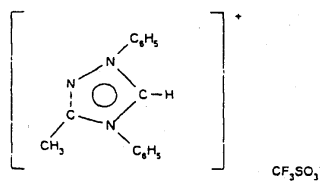
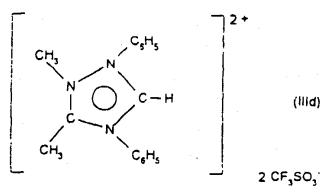
[J. Prakt. Chem., 1988, 330, 3, 325]

4 가 ,
1,2 - (IIIc) 2
50 %
:

- ^1H NMR (CD_3CN): δ 4.22 (s, 3H, CH_3N), 7.4-8.4
(미분해 피크, 페닐 H), 10.34 (s, 1H, H 사이클).

4. (IIId) :

IIId



[J. Prakt. Chem., 1988, 330, 3, 325]

1,2 - 3 2 가
(IIIId) 69 % 1,2 - 190.5 - 191.3

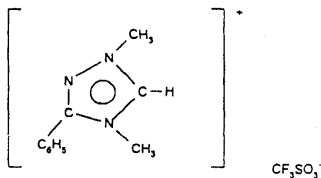
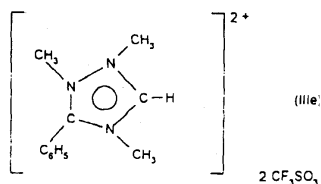
- ^1H NMR (CD_3CN): δ 3.04 (s, 3H, CH_3), 4.19 (s, 3H, CH_3N), 7.8-8.1 (미분해 피크, 10H, 1 페닐 H), 10.51 (s, 1H, H 사이클).

- ^{13}C NMR (CD_3CN): δ 12.31 (s, CH_3C), 38.04 (s, CH_3N), 126.70 (s, 2 페닐 CH), 128.02 (s, 페닐 C), 128.49 (s, 2 페닐 CH), 130.07 (s, 페닐 C), 131.56 (s, 2 페닐 CH), 131.83 (s, 2 페닐 CH), 134.04 (s, 1 페닐 CH), 135.88 (s, 1 페닐 CH), 120.35 (q, $^1J_{\text{CF}} = 320.1$ Hz, CF_3), 145.58 (s, CH 사이클), 157.66 (s, C 사이클 CH_3).

CH $^1J_{\text{CH}} = 240$ Hz

5. (IIIe) :

IIIe



[J. Prakt. Chem., 1988, 330, 3, 325]

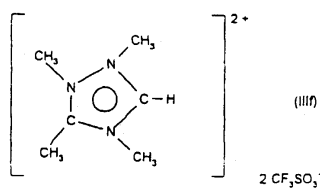
1,2 - 3 2 가
(IIIe) 71 % 1,2 - 180.0

:

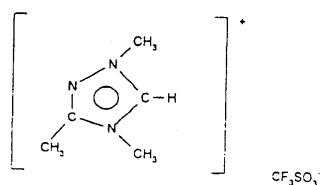
- ^1H NMR (CD_3CN): δ 4.08 (s, 3H, CH_3N), 4.20 (s, 3H, CH_3N), 4.46 (s, 3H, CH_3N), 7.8-8.1 (미분해 피크, 10H, 5 페닐 H), 10.16 (s, 1H, $\text{H}_{\text{사이클}}$).
- ^{13}C NMR (CD_3CN): δ 37.88 (s, CCH_3N), 38.36 (s, CH_3N), 39.42 (s, CH_3N), 130.78 (s, 페닐 C), 131.97 (s, 2 페닐 CH), 132.15 (s, 2 페닐 CH), 137.35 (s, 페닐 CH), 131.83 (s, 2 페닐 CH^-), 120.35 (q, $^1J_{\text{CF}} = 320.1$ Hz, CF_3), 147.35 (s, $\text{CH}_{\text{사이클}}$), 156.48 (s, $\text{C}_{\text{사이클}}$).

6. (III f) :

III f



, :



[J. Prakt. Chem., 1988, 330, 3, 325]

1,2 -

3

2

가

(III f)

95 %

1,2 -

194.4

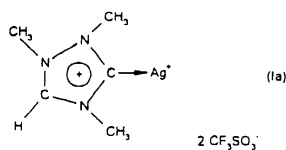
:

- ^1H NMR (d_6 -아세트론): δ 3.35 (s, 3H, CH_3C), 4.46 (s, 3H, CH_3N), 4.69 (s, 3H, CH_3N), 4.77 (s, 3H, CH_3N), 10.77 (s, 1H, $\text{H}_{\text{사이클}}$).
- ^{13}C NMR (d_6 -아세트론): δ 10.53 (s, CCH_3C), 35.91 (s, CH_3N), 36.26 (s, CH_3N), 37.99 (s, CH_3N), 120.35 (q, $^1J_{\text{CF}} = 320.1$ Hz, CF_3), 145.35 (s, $\text{CH}_{\text{사이클}}$), 157.31 (s, $\text{C}_{\text{사이클}}\text{CH}_3$).

(I)

7. Ag(I) (Ia) :

Ia



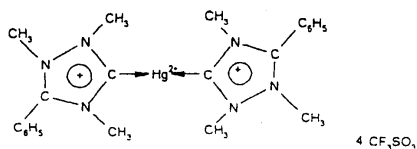
0.4 g (2.4 mmol) (THF) 1 (IIIa) 1 g
 가 . 2 . THF - , TH
 F 10 ml ((IIIa) 8
 2 %).

:

- ^1H NMR (CD_3CN): δ 4.01 (s, 3H, NCH_3), 4.19 (s, 3H, $\text{CH}_3\text{N}-\text{NCH}_3$), 4.22 (s, 3H, $\text{CH}_3\text{N}-\text{NCH}_3$), 9.72 (s, 1H, CH).
- ^{13}C NMR (CD_3CN): δ 37.2 (NCH_3), 38.5 (NCH_3), 38.6 (NCH_3), 121.1 (q, $^1J_{\text{CF}} = 320.1$ Hz, CF_3), 144.8 (CH), 189.2 (C_{Ag}).

8. Hg(II) (Ib) :

Ib



0.16 g (50 12) (DMSO) 1 ml
 (THF) 20 ml 5 (IIIe) 0.43 g 가 .
 24 . THF
 (IIIe) 86 % (Ib) 85.4 - 87

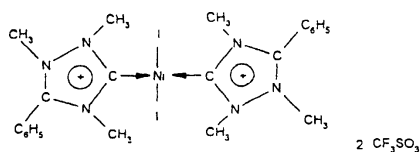
:

- ^1H NMR (CD_3OD): δ 4.70 (s, 12H, NCH_3 , $^4J_{\text{H-Hg}} = 12.8$), 4.29 (s, 6H, CH_3N , $^4J_{\text{H-Hg}} = 8.5$ Hz), 7.9-8.2 (미분해 피크, 10H, 페닐 H).
- ^{13}C NMR (CD_3OD): δ 38.79 ($\text{CH}_3\text{N}-\text{NCH}_3$), 41.75 (NCH_3), 121.1 (q, $^1J_{\text{CF}} = 320.1$ Hz, CF_3), 156.88 (C-Ph, $(^3J+^2J)_{\text{C-Hg}} = 86$ Hz), 183.78 (CHg , $^1J_{\text{CHg}} = 3275$ Hz).

X

9. Ni(II) (Ic) :

Ic



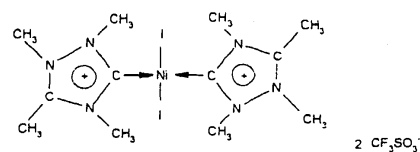
5 (IIIe) 2.4 g THF 50 ml 0.75 g
 0.442 g 가 2
 THF - 30 /
 (Ic) , 310.7 (:). (IIIe)
 85 %

- ^1H NMR (d_6 - 아세톤): δ 7.8-8.0 (br , 10H, 페닐 H),
 4.88-4.84 (2s, 6H, NCH_3), 4.54-4.49 (2s, 6H, CH_3N),
 4.42-4.41 (2s, 6H, CH_3N).
 - ^{13}C NMR (CD_3OD): δ 37.0 (CH_3N), 37.9 (CH_3N), 38.4
 (CH_3N), 121.1 (q, $^1J_{\text{CF}} = 320.1$ Hz, CF_3), 130.5, 130.8
 및 134.8 (페닐 C), 153.4 (C-Ph), 188.2 (C-Ni).

X

10. Ni(II) (Id) :

Id



6 (III f) 0.425g , 25 ml THF 0.090 g
 0.15 g 가 2
 THF 30 /
 (Id) , 300 - 305 (:).
 (III f) 79 %

:

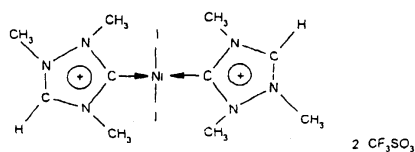
^1H NMR (d_6 -아세트론) : δ 4.88-4.84 (2s, 6H, NCH_3), 4.54-4.49 (2s, 6H, CH_3N), 4.42-4.41 (2s, 6H, CH_3N), 2.63 (s, 6H, C-CH_3).

- ^{13}C NMR (CD_3OD) : δ 13.86 (C-CH_3), 36.1 (CH_3N), 37.6 (CH_3N), 38.5 (CH_3N), 121.1 (q, $^1J_{\text{CF}} = 320.1$ Hz, CF_3), 154.8 (C-Me), 187.6 (C-Ni).

X

11.Ni(II) (Ie) :

Ie

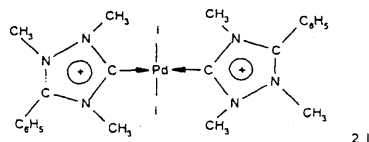


1 (IIIa) 0.935 g, 30 ml THF 0.200 g
0.34 g 가 2
THF
(Ie) (IIIa) 70 %

- ^1H NMR (d_6 -아세트론) : δ 4.38-4.35 (2s, 6H, CH_3N), 4.68-4.65 (2s, 6H, CH_3N), 4.99-4.96 (2s, 6H, NCH_3), 9.32 (s, 2H, CH).

12.Pd(II) (If) :

If



5 (IIIe) 0.472 g, 60 ml THF 0.112 g
0.30 g 가 2
(If) 30 /
211 - 213 (:

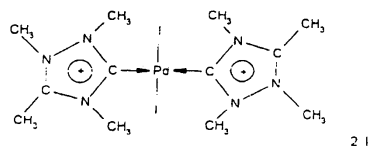
).
(IIIe) 51 %

- ^1H NMR (d_6 -DMSO): δ 7.8-8.1 (페닐, 10H, 페닐 H),
4.49-4.53 (2s, 6H, NCH_3), 4.21 (s, 6H, CH_3N), 4.10-4.13
(2s, 6H, CH_3N).
- ^{13}C NMR (d_6 -DMSO): δ 37.2 (CH_3N), 38.3 (CH_3N), 39.9
(CH_3N), 130.1, 130.9 and 134.5 (페닐 C), 152.4 (C-
Ph), 174.5 (C-Pd).

X

13.Pd(II) (Ig) :

Ig

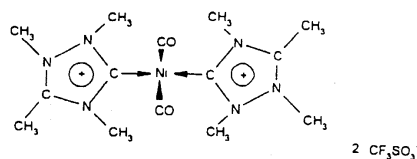


6 (IIIIf) 0.425 g, 60 ml THF 0.112 g
0.30 g 가 2
, 30 /
(Ig) 206 - 212 (
).
(IIIIf) 60 %

- ^1H NMR (d_6 -DMSO): δ 4.41-4.40 (2s, 6H, NCH_3), 4.29 (s,
6H, CH_3N), 4.16-4.15 (2s, 6H, CH_3N), 2.95 (6H, C- CH_3).

14.Ni(0) (Ih) :

Ih



A

1 ml 가 40 ml . 380 $\mu\ell$ 660 $\mu\ell$

60 ml 가 6 (III f) 2.0 g (點滴)

0 ml 가 (Ih) , 3 2 , 1 20

30 / (Ih) . (III f) 26 %

- ^1H NMR (d_6 -DMSO): δ 4.00 (s, 6H, NCH_3), 3.99 (s, 6H, CH_3N), 3.78 (s, 6H, CH_3N), 2.72 (6H, C-CH_3).

1982 cm^{-1} 1906 cm^{-1} (CO)

X

- 28.99 % (28.89 %)
- 3.36 % (3.63 %)
- 12.39 % (12.62 %)

B

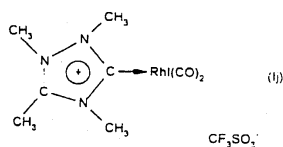
(Id) 0.2 g 150 mg (10) , 10 ml 10

가 A ((Id) 48 %

A , 가

15.Rh(I) (Ij) :

Ij



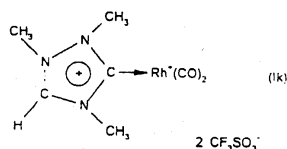
THF 10 ml () 0.277 g , THF 40 ml 6
 (III f) 0.456 g 0.16 g 가 50 2
 (III f) 70 %

- ^1H NMR (d_6 -DMSO): δ 4.47 (s, 3H, NCH_3), 4.28 (s, 3H, CH_3N), 4.20 (s, 3H, CH_3N), 2.96 (s, 3H, $\text{C}-\text{CH}_3$).
 - ^{13}C NMR (d_6 -DMSO): δ 10.5 (s, $\text{C}-\underline{\text{CH}_3}$), 35.2 (s, NCH_3), 36.8 (s, CH_3N), 37.9 (s, CH_3N), 154.2 (s, $\underline{\text{C}}-\text{CH}_3$), 183.0 (d, $^1\text{J}(\text{Rh}-\text{C}) = 82.9$ Hz, CO), 188.1 (d, $^1\text{J}(\text{Rh}-\text{C}) = 42.2$ Hz, 카르벤 C).

1975 cm^{-1} (CO)

16.Rh(I) (Ik) :

Ik



THF 10 ml () 0.200 g , THF 10 ml 1
 (III a) 0.16 g 가 50 15
 (III f) (Ik) 67 %

- ^1H NMR (d_6 -DMSO): δ 4.20 (s, 3H, NCH_3), 4.22 (s, 3H, CH_3N), 4.25 (s, 3H, CH_3N), 9.66 (s, 1H, CH).
 - ^{13}C NMR (d_6 -DMSO): δ 38.6 (s, NCH_3), 38.7 (s, NCH_3), 39.1 (s, CH_3N), 37.9 (s, CH_3N), 121.1 (q, $^1\text{J}_{\text{CF}} = 320.1$ Hz, CF_3), 145.5 (s, $\underline{\text{CH}}$), 186.1 (d, $^1\text{J}(\text{Rh}-\text{C}) = 76$ Hz, CO), 187.9 (d, $^1\text{J}(\text{Rh}-\text{C}) = 43.3$ Hz, 카르벤 C).

2029 (i) cm^{-1} 1985 (m) cm^{-1} (CO)

17.Rh(I) (Ij)

가 100 ml
 가
 Teflon ()
 Teflon () 15 Rh (I) (Ij) 40 mg 100 mg (15 ml,
 5) 5 ml 60 mg (4) (15)
 (15) 60 가 4
 / , 1
 (VPC)

- :
- : 95 %
 - : 97 %
 - / : 95/5
 - : 75 h^{-1} (, VPC)

18.Rh(I) (Ik)

16 (Ik) 40 mg 17
 80 3 / , 1
 (VPC)

- :
- : 96 %
 - : 100 %
 - / : 25/75
 - : 79 h^{-1} (, VPC)

(57)

1.

I , :

[I]

$[(Z^+ X^-)_m ML_n]Y$

(:

- Z^+ , , 1,2,4 - - 5 -

- L ,

- M 1b, 2b, 3b, 4b, 5b, 6b, 7b, 8 ,

- X^- ,

- m 1 6 ,

- n 0 5 ,

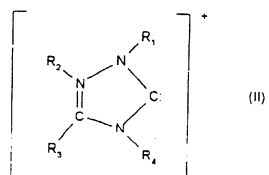
- m n 6 ,

- Y 가).

2.

1 , 1,2,4 - - 5 - Z^+ 가 II
:

[II]



[, R_1, R_2, R_3, R_4 , :

- ,

- ,

- , , , ,
:

- COOM_1 , $-\text{SO}_3\text{M}_1$, $-\text{PO}_3\text{M}_1$ (, M_1 , ,
- N(R)_4 (, R , 1 4
) ,

- $\text{N(R)}_3\text{Y}_a$ (, R 1 12
, Y_a) ,

- OH,

- COOM₁, -SO₃M₁, -PO₃M₁ (, M₁ , , 1 12
- N(R)₄ (, R , , 1 12
) ,

$$-N(R)_3 Y_a(\quad, R \quad, \quad, \quad, \quad, \quad),$$

- OH,

R_3 ,

R_1 / R_4 , 1,2,4 - - 5 -

, , , M

L , , ,

].

3.

1 2 , R₁ / R₄ , 1,2,4 - - 5

4.

5.

[illegible]

6.

1 5 , X - , 1,2,4 - - 5 -

7.

6. X^* 가

8.

III

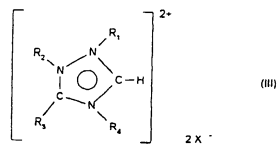
,

I

:

M

[III]



(,

- R_1, R_2, R_3, R_4

II 1,2,4 -

- 5 -

가 ,

- X^- I).

9.

8

,

,

25

150

,

M

,

III

가

,

.

10.

1

7

,

.

11.

10

,

,

(Heck)

,

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