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A New Study On Transition Metal Derivatives Of Ferrocene Pt-II

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ABSTRACT

Ferrocene on reaction with HgXCN [X= S, Se] forms 1,1′bis (thiocyanato/ selenocyanato) ferrocene. This compound acts as bidendate ligand and forms an adduct with $M(NCS)_2$ [M= Fe(II), Co(II), Ni(II), Cu(II), Zn(II)]. The bond length, bond order and bond angle of the ligands and the adducts have been evaluated with the help of Cache software. The bond length and bond angle indicate that basic structure of ferrocene is not altered after the formation of ligand or the adducts. The bidenlate nature of 1,1′bis(thiocyanato/selenocyanato) ferrocene is supported by the bond angles. The bond angles around M in various compounds is either 113 degree or 180 degree, which shows that M is well exposed for further reaction. The length of M-NCS bond changes on change of M which is the following order Zn > Cu > Ni > Fe > Co. This change has been attributed to the difference in the nature of sd hybridization.

KEYWORDS

Ferrocene derivatives;
Bond length;
Bond angle;
Computational study;
Transition metal derivatives.

INTRODUCTION

In our recent communication we have made new study on molecular structure of ferrocene[1] with the help of computational chemistry, using molecular mechanics method with EHT option. Ferrocene is well known compound and its crystographic structure was established in 1956[2]. About a decade ago we synthesized a large number of complexes of ferrocene derivatives and established their structures with the help of infrared, and electronic spectral studies, besides other physico-chemical techniques[3-11]. Crystographic structure of these complexes could not be performed for want of necessary requirements. The computational chemistry[12] and availability of software have made it possible to obtain such infor-

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mations about a molecule which were earlier possible only by crystographic study. The importance of bond length and bond angle in describing the nature of bonding in a compound has recently been emphasized[13]. We in this paper present a study on bond length and bond angles of a series of compounds of ferrocene.

MATERIAL AND METHOD

The compounds, which are study material of this paper, are listed in TABLE 1. These compounds have been prepared and studied by us in our earlier work[3-11]. For present study the 3D modeling and geometry optimization of all the compounds have been done with the help of PCMODEL software using the semiempirical PM3 Hamiltonian. The MOPAC calculation of bond length, bond order and bond angle were performed with Cache software. The optimized structure of compounds **(2)** and **(3)** is shown in figure 1 and of **(4-13)** is shown in figure-2.

TABLE 1

Compd. No.	Compounds
1	$Fe(C_5H_5)_2$
2	$Fe(C_5H_4)_2$-$(HgSCN)_2$
3	$Fe(C_5H_4)_2$-$(HgSeCN)_2$
4	$Fe(C_5H_4)_2$-$(HgSCN)_2.2Fe(NCS)_2$
5	$Fe(C_5H_4)_2$-$(HgSCN)_2.2Co(NCS)_2$
6	$Fe(C_5H_4)_2$-$(HgSCN)_2.2Ni(NCS)_2$
7	$Fe(C_5H_4)_2$-$(HgSCN)_2.2Cu(NCS)_2$
8	$Fe(C_5H_4)_2$-$(HgSCN)_2.2Zn(NCS)_2$
9	$Fe(C_5H_4)_2$-$(HgSeCN)_2.2Fe(NCS)_2$
10	$Fe(C_5H_4)_2$-$(HgSeCN)_2.2Co(NCS)_2$
11	$Fe(C_5H_4)_2$-$(HgSeCN)_2.2Ni(NCS)_2$
12	$Fe(C_5H_4)_2$-$(HgSeCN)_2.2Cu(NCS)_2$
13	$Fe(C_5H_4)_2$-$(HgSeCN)_2.2Zn(NCS)_2$

RESULT AND DISCUSSION

The first stage of the study is confined to the measurements of various bond length, bond order and bond angles of ferrocene followed by the same measurements of the 1,1′-bis(thiocyanato/selenocyanato mercurio) ferrocene (Figure-1) and of the adducts formed by reaction with M(NCS)2, [M=Fe(II), Co(II), Ni(II), Cu(II) and Zn (II)] (Figure-2). The compounds studied are listed in TABLE 1.

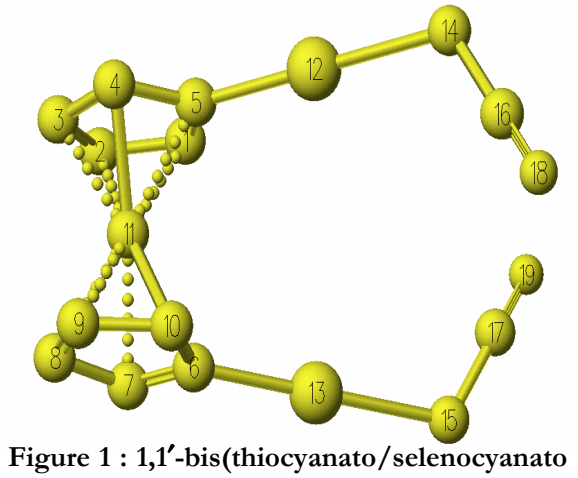

Figure 1 : 1,1′-bis(thiocyanato/selenocyanato mercuris) ferrocene (Compounds–2,3)

1–10 = Carbon 11 = Iron
12, 13 = Mercury 14, 15 = Sulphur or Selenium
16, 17 = Carbon 18, 19 = Nitrogen

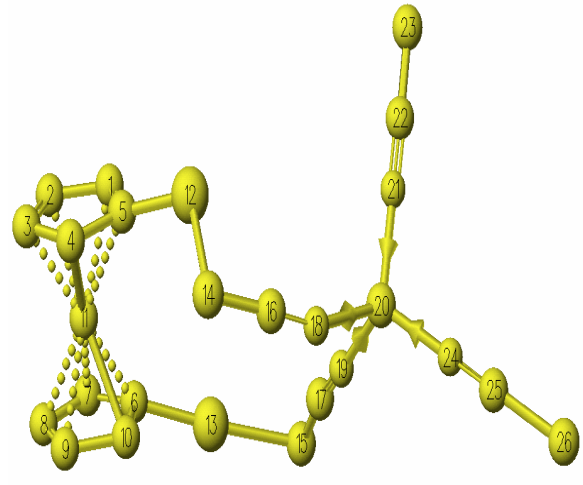

Figure 2: Complexes of 1,1′-bis(thiocyanato/seleno cyanato mercuris) ferrocene with $M(NCS)_2$ M=Fe(II), Co(II), Ni(II), Cu(II), Zn(II) (Compounds 4-13)

1 – 10 = Carbon 11 = Iron
12, 13 = Mercury 14, 15 = Sulphur or Selenium
16, 17 = Carbon 18, 19 = Nitrogen
20 = M 12, 24 = Nitrogen
22, 25 = Carbon 23, 26 = Sulphur

The computational result of bond length, bond order and bond angles of various bonds between C-C, and C-Fe of ferrocene are included in TABLE 3 which indicate that C-C bonds lengths are 1.540 Å

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TABLE 2

Bonds	Bond Length (Å)									
	Compound-4-8 1,1′-bis (mercurio thiocyanati) ferrocene					Compound- 5-13 1,1′-bis (mercurio thiocyanati) ferrocene				
	Fe	Co	Ni	Cu	Zn	Fe	Co	Ni	Cu	Zn
N_{18}-Fe_{20}	2.210	2.211	2.211	2.211	2.211	2.210	2.21	2.21	2.21	2.21
N_{19}-Fe_{20}	2.012	2.012	2.012	2.012	2.012	2.012	2.012	2.012	2.012	2.012
N_{21}-C_{22}	1.203	1.203	1.203	1.203	1.203	1.203	1.203	1.203	1.203	1.203
C_{22}-S_{23}	1.541	1.541	1.541	1.541	1.541	1.541	1.541	1.541	1.541	1.541
N_{24}-C_{25}	1.210	1.210	1.210	1.210	1.210	1.210	1.210	1.210	1.210	1.210
C_{25}-S_{26}	1.790	1.790	1.790	1.790	1.790	1.790	1.790	1.790	1.790	1.930
N_{21}-Fe_{20}	1.920	1.910	1.920	1.950	2.000	1.920	1.910	1.950	1.950	2.000
N_{24}-Fe_{20}	1.920	1.910	1.920	1.950	2.000	1.920	1.910	1.950	1.950	2.000
S_{23}-N_{21}	2.743	2.443	2.743	2.743	2.743	2.743	2.743	2.743	2.743	2.743

in six cases and 1.352 Å in four cases. Fe-C bonds have length in the range 2.2 Å in eight bonds and 2.1 Å in two cases. However, there is little difference in length in all the cases. The bond angles in ferrocene between C-C-C are very close to 109 degree C-Fe-C arte in the range of 35-40 degree.

On reaction with HgSCN and HgSeCN, the ferrocene is converted into 1,1′-bis(thiocyanato mercurio) ferrocene and 1,1′-bis(selenocyanato) ferrocene that is compound **(2)** and **(3)**. The bond length, bond order and bond angles are presented in the TABLE 4. The bond length, bond order and bond angles of various bonds of ferrocene remain intact and there is no change in them hence the bonds of ferrocene are not included in the TABLE. This observation supports the stability of the ferrocene.

The new bonds, which are created after the formation of compound of **(2)** and **(3)**, are the following:

C_5-Hg_{12}, C_6-Hg_{13}, Hg_{12}-X_{14}, Hg_{13}-X_{15}, X_{14}-C_{16}, X_{15}-C_{17}, C_{16}-N_{18}, C_{17}-N_{19}, X = S and Se

The bond lengths of the above bonds in thio and seleno derivatives have same length, but they differ in Hg-S, Hg-Se, C-S, C-Se bond lengths. The bond length between mercury and sulphur bond is 2.510 Å, between mercury and selenium bond is 2.650 Å, between sulphur and carbon is 1.790 Å and between selenium and carbon is 1.930 Å. The bond angles between Hg-S-C and Hg-Se-C are 120 degree; and between S-C-N, and Se-C-N are 180 degree.

On reaction with M $(NCS)_2$, [M =Fe(II), Co(II), Ni(II), Cu(II), Zn(II)] the 1,1′-bis(mercurio thiocyanato) ferrocene forms compounds no **(4-8)** and on reaction with its selenocyanate counterpart compound no. **(5-13)**. The bond length and bond order are included in TABLE 4 and 5 respectively. A compara-

TABLE 3: Bond length, bond order and bond angle of compound no. (1)

Bond	Bond Length (angstrom)	Bond Order	Labeled bond angle	Bond Angle (degree)
C1-C2	1.54	1.259	C3-Fe11-C4	41.232
C2-C3	1.352	1.248	C2-Fe11-C3	35.778
C3-C4	1.54	1.234	C2-Fe11-C1	40.234
C4-C5	1.54	1.268	C1-Fe11-C5	34.961
C5-C1	1.352	1.278	C5-Fe11-C4	40.612
C6-C7	1.352	1.274	C7-Fe11-C6	35.115
C7-C8	1.54	1.268	C6-Fe11-C10	40.274
C8-C9	1.352	1.259	C10-Fe11-C9	40.679
C9-C10	1.54	1.249	C9-Fe11-C8	35.692
C10-C6	1.54	1.234	C8-Fe11-C7	40.549
Fe11-C5	2.243	0.314	C1-C2-C3	109.061
Fe11-C1	2.258	0.317	C2-C3-C4	109.061
Fe11-C2	2.219	0.341	C3-C4-C5	103.755
Fe11-C3	2.181	0.367	C4-C5-C1	109.061
Fe11-C6	2.246	0.309	C5-C1-C2	109.061
Fe11-C7	2.235	0.304	C7-C8-C9	109.061
Fe11-C8	2.208	0.326	C8-C9-C10	109.061
Fe11-C4	2.193	0.35	C9-C10-C6	103.755
Fe11-C10	2.227	0.342	C10-C6-C7	109.061
Fe11-C9	2.203	0.345	C6-C7-C8	109.061

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TABLE 4: Bond length, bond order and bond angle (degree) of compound of compound no.(2-3) other than ferrocene ring

Nature of bond	Compound-2		Compound-3		Labeled bond angle	Compound-2	Compound-3
	Bond length	Bond order	Bond length	Bond order			
C5-Hg12	2.26	0.795	2.26	0.795	C7-C6-Hg13	125.469	125.469
C6-Hg13	2.26	0.912	2.26	0.912	C10-C6-Hg13	125.469	125.469
Hg12-S14	2.51	0.577	2.65	0.577	C6-Hg13-S15	180	180
Hg13-S15	2.51	0.832	2.65	0.832	C1-C5-Hg12	125.469	125.469
S14-C16	1.79	1.153	1.93	1.153	C4-C5-Hg12	125.469	125.469
S15-C17	1.79	1.094	1.93	1.094	C5-Hg12-S14	180	180
C16-N18	1.21	2.614	1.21	2.614	Hg13-S15-C17	120	120
C17-N19	1.21	2.645	1.21	2.645	Hg12-S14-C16	120	120
					S15-C17-N19	180	180
					S14-C16-N18	180	180

TABLE 5: Bond length and bond order of compound (4-8) other than ferrocene

Nature of bond	Compound 4		Compound 5		Compound 6		Compound 7		Compound 8	
	Bond length	Bond order	Bond length	Bond order	Bond length	Bond order	Bond length	Bond order	Bond length	Bond order
C5-Hg12	2.044	0.795	2.044	0.795	2.044	0.795	2.044	0.795	2.044	0.795
C6-Hg13	2.037	0.912	2.037	0.912	2.037	0.912	2.037	0.912	2.037	0.912
Hg12-S14	2.475	0.577	2.475	0.577	2.475	0.577	2.475	0.577	2.475	0.577
Hg13-S15	2.416	0.832	2.416	0.832	2.416	0.832	2.416	0.832	2.416	0.832
S14-C16	1.617	1.153	1.617	1.153	1.617	1.153	1.617	1.153	1.617	1.153
S15-C17	1.631	1.094	1.631	1.094	1.631	1.094	1.631	1.094	1.631	1.094
C16-N18	1.182	2.614	1.182	2.614	1.182	2.614	1.182	2.614	1.182	2.614
C17-N19	1.183	2.645	1.183	2.645	1.183	2.645	1.183	2.645	1.183	2.645
N18-Fe20	2.211	0.287	2.211	0.287	2.211	0.287	2.211	0.287	2.211	0.287
N19-Fe20	2.012	0.418	2.012	0.418	2.012	0.418	2.012	0.418	2.012	0.418
N21-C22	1.203	2.341	1.203	2.341	1.203	2.341	1.203	2.341	1.203	2.341
C22-S23	1.541	1.468	1.541	1.468	1.541	1.468	1.541	1.468	1.541	1.468
N24-C25	1.21	2.589	1.21	2.589	1.21	2.589	1.21	2.589	1.21	2.589
C25-S26	1.79	1.158	1.79	1.158	1.79	1.158	1.79	1.158	1.79	1.158
N21-Fe20	1.92	0.491	1.91	0.491	1.92	0.491	1.95	0.491	2.00	0.491
N24-Fe20	1.92	0.328	1.91	0.328	1.92	0.328	1.95	0.328	2.00	0.328
S23-N21	2.743	0.337	2.743	0.337	2.743	0.337	2.743	0.337	2.743	0.337

tive display of bond length is given in TABLE 2.

The length of metal nitrogen bonds, N_{18}-M_{20} and N_{19}-M_{20} [Metal = Fe (II), Co(II), Ni (II), Cu (II), Zn (II)] in all the cases are 2.012 and 2.211 Å indicating very clearly that there is no change in length on change of the metal ions. Similarly there are no changes in the length in other bond shown in the TABLE 2. A notable change in the length of metal bonds N_{21}-M_{20}, and N_{24}-M_{20} is however, observed. The smallest bond is of Co-N, followed by Fe-N and Ni-N; the longest bond is of Zn-N. The sequence is as below:

Zn-N > Cu > N > Ni-N ~ Co-N > Fe-N

The bond angles involving the metal ions are the following and are presented in TABLE 7 for compounds no. **(4-13)**.

Bond Angles

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TABLE 6: Bond length and bond order of compound (9-13) other than ferrocene

Nature of bond	Compound 9		Compound 10		Compound 11		Compound 12		Compound 13	
	Bond length	Bond order	Bond length	Bond order	Bond length	Bond order	Bond length	Bond order	Bond length	Bond order
C5-Hg12	2.044	0.795	2.044	0.795	2.044	0.795	2.044	0.795	2.044	0.795
C6-Hg13	2.037	0.912	2.037	0.912	2.037	0.912	2.037	0.912	2.037	0.912
Hg12-Se14	2.475	0.577	2.475	0.577	2.475	0.577	2.475	0.577	2.475	0.577
Hg13-Se15	2.416	0.832	2.416	0.832	2.416	0.832	2.416	0.832	2.416	0.832
Se14-C16	1.617	1.153	1.617	1.153	1.617	1.153	1.617	1.153	1.617	1.153
Se15-C17	1.631	1.094	1.631	1.094	1.631	1.094	1.631	1.094	1.631	1.094
C16-N18	1.182	2.614	1.182	2.614	1.182	2.614	1.182	2.614	1.182	2.614
C17-N19	1.183	2.645	1.183	2.645	1.183	2.645	1.183	2.645	1.183	2.645
N18-Fe20	2.211	0.287	2.211	0.287	2.211	0.287	2.211	0.287	2.211	0.287
N19-Fe20	2.012	0.418	2.012	0.418	2.012	0.418	2.012	0.418	2.012	0.418
N21-C22	1.203	2.341	1.203	2.341	1.203	2.341	1.203	2.341	1.203	2.341
C22-Se23	1.541	1.468	1.541	1.468	1.541	1.468	1.541	1.468	1.541	1.468
N24-C25	1.21	2.589	1.21	2.589	1.21	2.589	1.21	2.589	1.21	2.589
C25-Se26	1.93	1.158	1.93	1.158	1.93	1.158	1.93	1.158	1.93	1.158
N21-Fe20	1.92	0.491	1.91	0.491	1.92	0.491	1.95	0.491	2	0.491
N24-Fe20	1.92	0.328	1.91	0.328	1.92	0.328	1.95	0.328	2	0.328
Fe11-C9	2.203	0.345	2.203	0.345	2.203	0.345	2.203	0.345	2.203	0.345
Se23-N21	2.743	0.337	2.743	0.337	2.743	0.337	2.743	0.337	2.743	0.337

TABLE 7: Bond angles (degree) of compounds no. (4-13) other than ferrocene ring

Labeled bond angles	Compd. 4	Compd. 5	Compd. 6	Compd. 7	Compd. 8	Compd. 9	Compd. 10	Compd. 11	Compd. 12	Compd. 13
C7-C6-Hg13	144.668	144.668	144.668	144.668	144.668	144.668	144.668	144.668	144.668	144.668
C10-C6-Hg13	101.208	101.208	101.208	101.208	101.208	101.208	101.208	101.208	101.208	101.208
C6-Hg13-S15	176.701	176.701	176.701	176.701	176.701	176.701	176.701	176.701	176.701	176.701
C1-C5-Hg12	132.568	132.568	132.568	132.568	132.568	132.568	132.568	132.568	132.568	132.568
C4-C5-Hg12	116.567	116.567	116.567	116.567	116.567	116.567	116.567	116.567	116.567	116.567
C5-Hg12-S14	118.916	118.916	118.916	118.916	118.916	118.916	118.916	118.916	118.916	118.916
Hg13-S15-C17	92.52	92.52	92.52	92.52	92.52	92.52	92.52	92.52	92.52	92.52
Hg12-S14-C16	92.778	92.778	92.778	92.778	92.778	92.778	92.778	92.778	92.778	92.778
S15-C17-N19	170.966	170.966	170.966	170.966	170.966	170.966	170.966	170.966	170.966	170.966
C17-N19-Fe20	173.99	173.99	173.99	173.99	173.99	173.99	173.99	173.99	173.99	173.99
S26-C25-N24	180.00	180.00	180.00	180.00	180.00	180.00	180.00	180.00	180.00	180.00
C25-N24-Fe20	180.00	180.00	180.00	180.00	180.00	180.00	180.00	180.00	180.00	180.00
S14-C16-N18	178.195	178.195	178.195	178.195	178.195	178.195	178.195	178.195	178.195	178.195
C16-N18-Fe20	150.438	150.438	150.438	150.438	150.438	150.438	150.438	150.438	150.438	150.438
N18-Fe20-N24	113.497	113.497	113.497	113.497	113.497	113.497	113.497	113.497	113.497	113.497
N24-Fe20-N19	113.497	113.497	113.497	113.497	113.497	113.497	113.497	113.497	113.497	113.497
N21-Fe20-N19	113.497	113.497	113.497	113.497	113.497	113.497	113.497	113.497	113.497	113.497
Fe20-N21-C22	180.00	180.00	180.00	180.00	180.00	180.00	180.00	180.00	180.00	180.00
N21-C22-S23	178.961	178.962	178.961	178.961	178.962	178.961	178.962	178.961	178.961	178.962

C_{17}-N19-M_{20} C_{25}-N_{24}-M_{20} C_{16}-N_{18}-M_{20}
N_{18}-M_{20}-N_{24} N_{24}-M_{20}-N_{19} N_{21}-M_{20}-N_{19} M_{20}-N_{21}-C_{22}

The angles cited above are the same in all the cases, irrespective of the metal ions. The angles between N_{19}-M_{20}-N_{21}, N_{19}-M_{20}-N_{24} and N_{18}-M_{20}-N_{24} are 113.449 degree. This angle is close to angle prescribed for tetrahedron, which is 109.5 degree. The metal ions are supposed to be linked to thiocyanate ions in geometry close to tetrahedron.

The compounds **(9-13)** are formed when 1,1′bis (seleno cyanato mercurio) ferrocene is reacted with $M(NCS)_2$. The bond length of C_{25}-Se_{26} becomes 1.932 Å against 1.790 Å in the corresponding sulphur derivative. In other bonds there is no noticeable change. The relevant bond angles as presented above for thiocyanato analogues exhibit no change on change of metal ion [M = Fe (II), Co (II), Ni (II), Cu (II), Zn (II)] or on change of sulphur to selenium.

The metal ligand bond length and its relation with hybridization has been discussed by Hehre[14] and other[15,16]. He has ignored the contribution of p orbitals in hybridization, which is in consonance with the work of the Landis[17] and Kaup[18] and others[19-22]. Our observation clearly shows that on change of M, the length of both M-NCS bonds changes, the longest being Zn-NCS bond and smallest being Co-NCS bond. This change is on account of difference in the nature of sd-hybridization.

CONCLUSION

1. The bond order of carbon-iron bond in ferrocene is 0.314, whereas the bond order of carbon-carbon bond is 1.25 or more. The difference in bond order indicates that former has sigma bonding and the latter pi boding.
2. The carbon in cyclopentadienyl radical has sp^3 hybridization as is indicated by C-C-C, angle which is 109 degree.
3. On change of M the length of both M-NCS bonds changes, the longest is when M is Zn, and the sequence is Zn > Cu > Ni ~ Fe > Co.
4. In compound no. **(2)**, the angle between both the Hg-S-C is 120 degree, which provides a comfortable orientation for acting as bidentate ligand.
5. The bond angles around M in compound **(4-13)**, are above 113 degree, and some are close to 180 degree, which shows that M is well exposed for further reaction.

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REFERENCES

[1] P.P.Singh, V.B.L.Srivastava, Deepa Singh; Inorg.Chem. I.J., (In press).
[2] R.C.Mehrotra, A.Singh; Organo Metallic Chemistry Wiley Eastern Ltd, 247 **(1992)**.
[3] P.P.Singh, D.S.Gupta; Polyhedron, **5**, 1941 **(1986)**.
[4] P.P.Singh, Divya Singh, N.B.Singh; Bull.Chem.Soc.Jpn **61**, 4417 **(1988)**.
[5] P.P.Singh, Divya Singh; Synth.React.Met.Org.Chem., **15**, 1219 **(1985)**.
[6] P.P.Singh, D.S.Gupta, N.B.Singh; Synth.React.Met.Org. Chem., 361 **(1987)**.
[7] P.P.Singh, N.B.Singh; Polyhedron, **9**, 557 **(1990)**.
[8] P.P.Singh, N.B.Singh, D.S.Gupta; Synth.React.Met.Org. Chem., **22**, 905 **(1992)**.
[9] P.P.Singh, N.B.Singh, D.S.Gupta; Proc.Nat.Acad.Sci., India, **62(A)**, 353 **(1992)**.
[10] P.P.Singh, Deepa Singh, A.P.Singh; Int.J.Chem., **34(A)**, 472 **(1995)**.
[11] P.P.Singh, Deepa Singh, A.P.Singh; Int.J.Chem., **34(A)**, 476 **(1995)**.
[12] E.R.David; Chem.Rev., **100**, 351 **(2000)**.
[13] G.Frenking, N.Frohlich; Chem.Rev., **100**, 717 **(2000)**.
[14] K.D.Dobbs, W.J.Hehre; J.Am.Chem.Soc., **108**, 4663 **(1986)**.
[15] L.J.Gaggenberger, R.R.Schyock; J.Am.Chem.Soc., **97**, 6578 **(1975)**.
[16] M.R.Churchill, W.J.Young; Inorg.Chem., **18**, 171 **(1979)**.
[17] C.R.Landis, T.K.Firman; J.Am.Chem.Soc., **120**, 2641 **(1998)**.
[18] M.Kaupp; Chem.Eur.J., **5**, 3631 **(1999)**.
[19] W.P.Griffith, T.D.Wickings; J.Chem.Soc.A, 400 **(1968)**.
[20] R.Tatsumi, R.Hoffmann; Inorg.Chem., **19**, 2656 **(1980)**.
[21] D.M.P.Mingos; J.Organomet.Chem., **179**, C29 **(1979)**.
[22] (a) D.C.Brower, J.L.Templeton, D.M.P.Mingos; J.Am. Chem.Soc., **109**, 5203 **(1987)**.
(b) P.J.Pyykkö; Phys.Chem.A, **101**, 8017 **(1997)**.