Journal of Advances in Science and Technology

Vol. IV, No. VII, November-2012, ISSN 2230-9659

TRIPHENYL SILICON (IV) COMPLEXES OF 1-PHENYL-3-ARYL PYRAZOLE-4-CARBOXALDEHYDE THIOSEMICARBAZONES AND SEMICARBAZONES

www.ignited.in

Journal of Advances in Science and Technology
Vol. IV, No. VII, November-2012, ISSN 2230-9659

Triphenyl Silicon (IV) Complexes of 1-Phenyl-3-Aryl Pyrazole-4-Carboxaldehyde Thiosemicarbazones and Semicarbazones

Durga Prasad Mohanty[1], Dr. K. P. Singh[2]

[1]Research Scholar, Monad University, Pilkhua (Hapur), Ghaziabad

[2]Professor, Deptt. Of Chemistry, NIT Engg. College, Greater Noida, Noida

Abstract – Derivatives of the types R-CH=N-NH-CX-NH$_2$ and RRC=N-NH-CX-NH$_2$ which are usually obtained by condensation of thiosemicarbazide or semicarbazide with suitable aldehydes and ketones, are named by adding 'thiosemicarbazone' (X = S) or 'semicarbazone' (X = O) after the name of the condensed aldehyde or ketone. It is usual also to include in this class derivatives with substituents on the amide or thioamide nitrogen, on the X atom, or on the 'hydrazinic' nitrogen.[146]

Thiosemicarbazones (TSC) and semicarbazones (SC) are amongst the most widely studied nitrogen and sulfur/oxygen donor legends. These classes of compounds usually react with metallic cations giving complexes in which the TSC and SC behave as chelating ligands. Research on the coordination chemistry, analytical applications and biological activities of these complexes has increased steadily for many years. These compounds have remarkable biological activities ranging from anti-protozoa, antibacterial, antifungal, antitumoral,antiviral activities and specially anti-HIV activity,which have since been shown to be related to their metal complexing ability.

Key words: condensation, legends, coordination chemistry, analytical applications.

◆

INTRODUCTION

In free unsubstituted TSC and SC in solid state the C=N-NH-CX-NH$_2$ backbone is usually planar, with the X (S, O) atom *trans* to the azomethine N. Although there are several electronic and steric factors that may contribute to the adoption of this arrangement, the most important is probably that the *trans* arrangement places the amine and azomethine nitrogen atoms in relative positions suitable for intramolecular hydrogen bonding. TSC and SC are versatile ligands in both neutral and anionic forms, having interesting coordination properties. The coordination behavior exhibited by TSC is considerably more varied than the simple monodentate coordination allowed by the configuration of the free ligands or the N(3),S-chelation which becomes possible when the *Z*-configuration is adopted with respect to the N(2)-C(1) bond. The coordination modes that have been described are summarized in Fig.-2.6, as regards the ligand-metal bonds involving the thiosemicarbazide chain. The elements of Group 12 form complexes in which the ligand adopts coordination modes (I-IV). The two first modes occurs in adducts with metal halides, while N(1),N(3)-coordination (mode III) occurs in S-alkylated ligands. The common place N(3),S-coordination of the thiosemicarbazonate anion in *Z*-configuration mode (IV) is illustrated by several examples. Group 14 adds another mode (V), monodentate coordination by a deprotonated TSC; in this mode, found in the complex of triphenyltin(IV) with salicylaldehyde thiosemicarbazone, there is no bridging by the S atom, possibly because of steric hindrance by the bulky phenyl groups.

REVIEW OF LITERATURE

The structures of Group 13 metal thiosemicarbazonates exhibit several coordination modes.[147] The metallic and organometallic ions of this group are able to use simultaneously all the potential donors of both *E* and *Z*-TSC chains. Coordination modes (VI-IX) are particularly associated with the complexes of this group, although some of the preceding modes also occur. In mode (VI) there is four-membered metallacycle, while coordination modes (VII) and (VIII) use all the donor atoms of the deprotonated TSC chain. Finally, mode (IX) consists in rather unusual monodentate bridging behavior; it has been found only in a complex of the $TlMe_2^+$ cation with pyridoxal thiosemicarbazone in which the expected coordination via N(3) may be blocked by a strong hydrogen bond between N(3) and the pyridoxal phenolic hydroxyl group.

In the SC complexes the ligands show simpler coordination behavior than TSC. All adopt the chelating modes (X) and (XI), which are equivalent to

TSC modes (II) and (IV), respectively, and becomes possible when the *E*-conformation of the free ligand changes to *Z*-conformation. In modes (II) and (X), the thiosemicarbazones and semicarbazones contain non-deprotonated TSC and SC, so the coordination bonds indicated involve the lone pairs of the N(3) and sulfur/oxygen atoms.

MATERIAL AND METHOD

Whereas in the modes (IV) and (XI), only β-nitrogen coordinates to the metal atom, while the α-nitrogen atom remains uncoordinated. On the other hand, remaining sulfur/oxygen atom has a tendency to form a strong covalent bond with metal atom. Although the proton lost by the anions formally belongs to the hydrazinic NH group, the anion is usually represented in the canonical thiol form and usually in *Z*-configuration (Fig.-2.6).

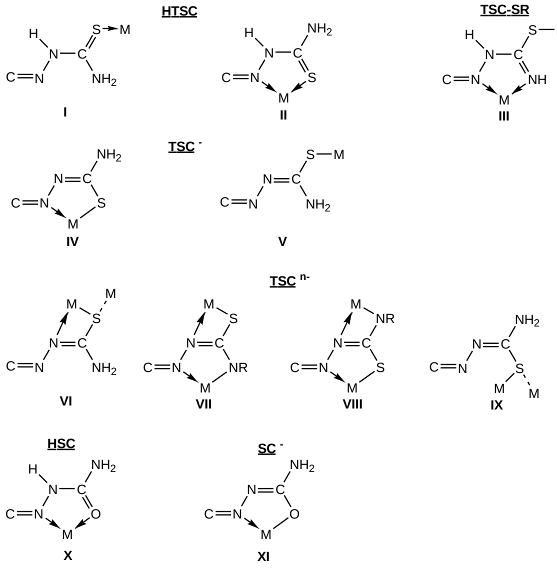


Fig.-2.6

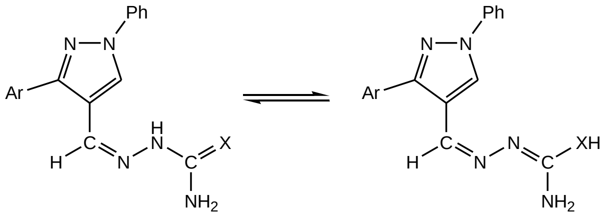
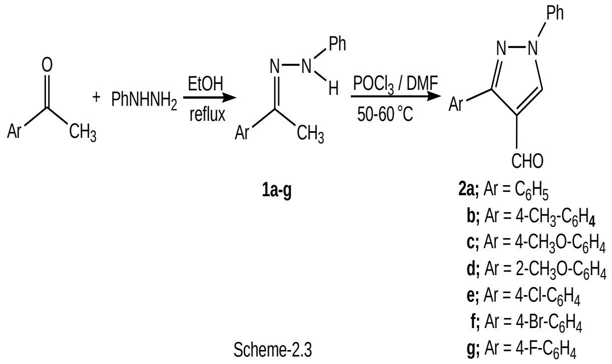


Fig.-2.7

Synthesis of 1-phenyl-3-arylpyrazole-4-carboxaldehydes 1-Phenyl-3-arylpyrazole-4-carboxaldehydes (2a-g) were prepared in two steps. The first one was the condensation reaction between acetophenone derivatives and phenyl hydrazine to give the corresponding acetophenone phenyl hydrazone derivatives (1a-g). The hydrazone derivatives were treated with cold solution of dimethylformamide and phosphorus oxychloride (Vilsmeier-Haack reagent),[163] followed by neutralization with sodium bicarbonate, leading to the corresponding 4-carboxaldehyde functionalized pyrazole heterocyclic ring in mild operating conditions. The compounds 2a-g were identified by IR and ^{1}H NMR spectra.



Scheme-2.3

CONCLUSION

The organosilicon(IV) compounds have versatile applicability in pharmaceutical and in chemical industries. On the other hand, substituted pyrazole ring also exhibited a broad spectrum of biological activities such as antidiabetic,[156] antimicrobial[157-160] and herbicidal.[161,162] Moreover in many cases, by coordination to different transition metal ions that can be found in biological systems, it is possible to obtain complexes that are more efficient drugs than the corresponding free ligands. So, the present situation prompted us to produce such work with azomethine moieties in which the combined effect of silicon along with plus role of pyrazole ring and sulfur/oxygen is applicable. Therefore, we carried out a study of the reactions of triphenylchlorosilane with the 1-phenyl-3-arylpyrazole-4-carboxaldehyde thiosemicarbazone and semicarbazone ligands, which have been shown to exist in tautomeric forms (Fig.-2.7).

REFERENCES

1. C. Chuit, R.J.P. Corriu, C. Reye and J.C. Young, *Chem. Rev.*, 93, 1371 (1993).

2. R.R. Holmes, *Chem. Rev.,* 96, 927 (1996).

3. M.A. Brook, *Extracoordination at Silicon. Silicon in Organic, Organometallic and Polymer Chemistry*, Wiley: New York, 2000, p 97.

4. M.G. Voronkov, O.M. Trofimova, Y.I. Bolgova and N.F. Chernov, *Russ. Chem. Rev.*, 76, 825 (2007).

5. M. Benaglia, S. Guizzetti and L. Pignataro, *Coord. Chem. Rev.*, 252, 492 (2008).

6. D. Kost and I. Kalikhman, *Acc. Chem. Res.,* 42, 303 (2009).

7. S. Rendler and M. Oestreich, *Synthesis,* 1727 (2005).

8. Y. Orito and M. Nakajima, *Synthesis,* 1391 (2006).

9. S.E. Denmark, Y. Fan and M.D. Eastgate, *J. Org. Chem.*, 70, 5235 (2005).

10. D. Seyferth, *Organometallics,* 20, 4978 (2001).

11. J. Acker and K. Bohmhammel, *J. Phys. Chem. B,* 106, 5105 (2002).

12. G. Maier, J. Glatthaar and H.P. Reisenauer, *J. Organomet. Chem.,* 686, 341 (2003).

13. J. Acker and K. Bohmhammel, *J. Organomet. Chem.,* 693, 2483 (2008).

14. Y. Na and S. Chang, *Org. Lett.,* 2, 1887 (2000).

15. J.F. Jenson, B.Y. Svendsen, T.V.L. Cour, H.L. Pederson and M. Johannsen, *J. Am. Chem. Soc.,* 124, 4558 (2002).

16. S.H. Kang, J.S. Han, W.C. Lim, I.N. Jung, M.E. Lee and B.R. Yoo, *Organometallics,* 25, 318 (2006).

17. B.H. Lipshutz, N. Tanaka, B.R. Taft and C.T. Lee, *Org. Lett.,* 8, 1963 (2006).

18. E. Calimano and T.D. Tilley, *J. Am. Chem. Soc.,* 131, 11161 (2009).

19. A.K. Roy, *Adv. Organomet. Chem.*, 55, 1 (2007).

20. S.T. Phan, W.C. Lim, J.S. Han, I.N. Jung and B.R. Yoo, *J. Organomet. Chem.,* 691, 604 (2006).

21. S.D. Gonzalez and L. Blanco, *J. Organomet. Chem.,* 693, 2033 (2008).

22. F. Li and W.R. Roush, *Org. Lett.,* 11, 2932 (2009).

23. A. Postigo, S. Kopsov, S.S. Zlotsky, C. Ferreri and C. Chatgilialoglu, *Organometallics,* 28, 3282 (2009).

24. D.C. Pestana, T.S. Koloski and D.H. Berry, *Organometallics,* 13, 4173 (1994).

25. S.K. Grumbine and T.D. Tilley, *J. Am. Chem. Soc.,* 116, 6951 (1994).

26. J. Terao, H. Watabe, H. Watanabe and N. Kambe, *Adv. Synth. Catal*., 346, 1674 (2004).

27. J. Terao and N. Kambe, *Chem. Rec.,* 7, 57 (2007).

28. K. Murakami, K. Hirano, H. Yorimitsu and K. Oshima, *Angew. Chem. Int. Ed.,* 47, 5833 (2008).

29. E. Morita, K. Murakami, M. Iwasaki, K. Hirano, H. Yorimitsu and K. Oshima, *Bull. Chem. Soc. Jpn.,* 82, 1012 (2009).

30. W. Uhlig, *J. Organomet. Chem.,* 685, 70 (2003).

31. J. Harloff, E. Popowski and H. Reinke, *J. Organomet. Chem.,* 692, 1421 (2007).

32. A.D. Dilman, V.V. Levin, A.A. Korlyukov, P.A. Belyakov, M.I. Struchkova, M.Y. Antipin and V.A. Tartakovsky, *J. Organomet. Chem.,* 693, 1005 (2008).

33. A.A. Korlyukov, K.A. Lyssenko, M.Y. Antipin, E.A. Grebneva, A.I. Albanov, O.M. Trofimova, E.A. Zelbst and M.G. Voronkov, *J. Organomet. Chem.,* 694, 607 (2009).

34. S.G. Shevchenko, Y.L. Frolov, A.V. Abramov and M.G. Voronkov, *J. Organomet. Chem.,* 690, 2922 (2005).

35. U.H. Berlekamp, A. Mix, B. Neumann, H.G. Stammler and P. Jutzi, *J. Organomet. Chem*., 667, 167 (2003).

36. M.G. Voronkov, O.M. Trofimova, N.F. Chernov, A.I. Albanov, N.N. Chipanina and A. Grebneva, *Appl. Organomet. Chem.,* 19, 538 (2005).

37. A.R. Bassindale, M. Borbaruah, S.J. Glynn, D.J. Parker and P.G. Taylor, *J. Organomet. Chem.,* 606, 125 (2000).

38. A.G. Shipov, E.P. Kramarova, E.A. Mamaeva, O.A. Zamyshlyaeva, V.V. Negrebetsky, Y.E. Ovchinnikov, S.A. Pogozhikh, A.R. Bassindale, P.G. Taylor and Y.I. Baukov, *J. Organomet. Chem.,* 620, 139 (2001).

39. A.R. Bassindale, Y.I. Baukov, P.G. Taylor and V.V. Negrebetsky, *J. Organomet. Chem.,* 655, 1 (2002).

40. V.V. Negrebetsky, P.G. Taylor, E.P. Kramarova, S.Y. Bylikin, I.Y. Belavin, A.G. Shipov, A.R. Bassindale and Y.I. Baukov, *J. Organomet. Chem.,* 691, 3976 (2006).