

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly, Peer Reviewed Journal)

Visit: www.ijirset.com

Vol. 7, Issue 2, February 2018

pH METRIC STUDIES OF COMPLEXES OF Ni (II) WITH N-ACETYL BENZENESULPHONAMIDE AND N-ACETYL-P-TOLUENESULPHONAMIDE

Dr. Shilpi Deep Mathur

Associate Professor, Dept. of Chemistry, Rameshwari Devi Girls College, Bharatpur, Rajasthan, India

ABSTRACT: Stock solution of the nickel ($\sim 0.01 \text{ mol}\cdot\text{L}^{-1}$) used in the study was prepared from the nitrate salt of $(\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O})$. This stock solution was acidified with HCl to prevent the hydrolysis of the metal, and concentration of the acid solution was determined through Gran method potentiometrically [15]. Concentration of the Ni(II) solution was determined by complexometric EDTA titration [15–17]. Potassium hydrogen phthalate was used to standardize carbonate-free sodium hydroxide (titrant, prepared in $0.1 \text{ mol}\cdot\text{L}^{-1}$ KNO_3 solution) potentiometrically [18, 19]. The amino acids (L-Asp (98%), L-Glu (99.5%), L-Asn (98%), L-Leu (98%), L-Phe (98%), and L-Trp (98%)) and adenine (99%) were used as received. An HCl solution ($0.1 \text{ mol}\cdot\text{L}^{-1}$) was prepared and used after standardization as described [20]. All of the solutions used during the experiments were prepared freshly in ultra pure water having a resistivity of $18.3 \text{ mol}\cdot\text{L}^{-1}\Omega \text{ cm}$. Samples of all of the aqueous solutions were prepared gravimetrically.

KEYWORDS: Ni(II), n-acetylbenzenesulphonamide, n-acetyl-p-toluenesulphonamide, pH metric, complexes

I. INTRODUCTION

Adenine was titrated alone and in the presence of Ni(II) ion potentiometrically. Potentiometric titration curve of the Ni(II):Ade system, curve II. The decrease in the pH value of the reaction mixture indicated that Ni(II):Ade complexes form at 1 : 1 and 1 : 2 mol ratios for (1 : 1) and curve III for (1 : 2) binary complexes of Ni(II):Ade, respectively.¹ Hamada et al. demonstrated in their work that large metal ions (such as Cd(II) or Hg(II) with ionic radius = 95 and 102 pm, resp.) will coordinate in a chelate fashion between the N(3) and N(9) in adenine. Smaller metal ions (74 pm) will fit in the smaller chelate ring between the N(7) and N(10) in adenine.² The stability constants of these complexes, which were formed, were calculated (according to (1) and (2)) at $0.1 \text{ mol}\cdot\text{L}^{-1}$ KNO_3 ionic medium and 25.0°C temperature with BEST computer program. From these results,³ it was seen that the results presented in the previous literature were coherent with the values of this research.⁴

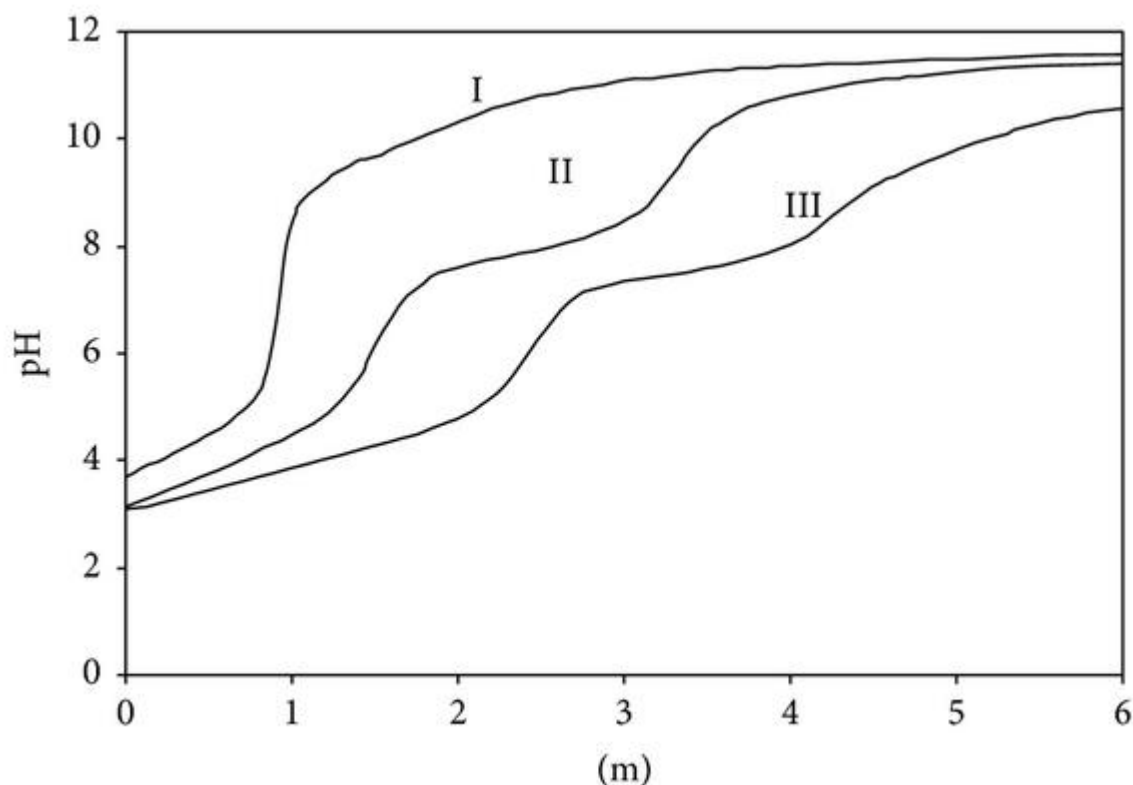
Potentiometric titrations of each amino acid selected for this study were performed alone, and also in the presence of Ni(II) ion in aqueous solution in (1 : 1) to (1 : 3) stoichiometry, at $0.1 \text{ mol}\cdot\text{L}^{-1}$ KNO_3 ionic medium, 25.0°C , in nitrogen atmosphere.⁵ Instead of giving potentiometric titration curves for all Ni(II):L-amino acid reactions, only Ni(II):L-aspartic acid curves were given for simplicity (Figure 3). In Figures 2–4, m in -axis represents mmole base/mmole metal or mmole base/mmole ligand. In order to calculate the stability constants of Ni(II) ion with L-amino acids used in this study, protonation constants given in Table 1 were used [23]. The stability constants of binary coordination complexes of Ni(II) with L-amino acids determined in this study.⁶ Literature values on the stability constants of binary complexes of Ni(II):L-amino acids⁷ for comparison [36–41]. It can be seen that Ni(II) ion forms coordination complexes at 1 : 1 and 1 : 2 mole ratios with L-Asp and L-Leu, respectively. It is also clear that Ni(II) ion forms 1 : 1, 1 : 2, and 1 : 3 coordination compounds with L-Glu, L-Asn, L-Phe, and L-Trp.⁸

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly, Peer Reviewed Journal)

Visit: www.ijirset.com

Vol. 7, Issue 2, February 2018



The stability constants of the ternary complexes of Ni(II) ions that form between Ni(II):Ade:L-amino acids at 1 : 1 : 1 mole ratio were calculated from the potentiometric titration results. As in the binary complexes, instead of giving the graphical results for all of the ternary complexes, potentiometric titration curves for the ternary complex of Ni(II):Ade:L-asp were given as an example for simplicity. Ni(II):L-Asp binary complex begins to form at pH = 3. It reaches maximum level (15%) at pH = 4.1, and Ni(II):L-Asp complex disappears completely at pH = 7 in this aqueous solution (shown as NiB in Figure 5). Ni(II):Ade:L-Asp ternary complex begins to form at pH = 3. It reaches its maximum level (95%) at pH = 6 (shown as NiAB in Figure 5). Ni(II):Ade:L-Asp ternary complex remains stable as dominant complex in this aqueous solution between pH 6 and pH 10.⁹

Ni(II):Ade binary complex forms at very low levels at pH = 4–8 (Figure 6). At the same pH levels, Ni(II):Ade:L-Glu ternary complexes begin to form. The level of this complex reaches its maximum level (100%) at pH = 7¹⁰

Ni(II):Ade:L-Asn ternary complex formation reactions were also investigated in aqueous solution. As it can be seen in Figure 7, Ni(II):L-Asn binary complexes 1 : 1 and 1 : 2 form at pH 2–6. In addition, it may be seen that Ni(II):Ade:L-Asn complex begins to form at pH = 2, and it reaches its maximum level (99%) at pH 6.¹¹

The diagrams drawn for the Ni(II):Ade:L-Leu ternary system showed a different behavior from other ternary systems analyzed in this research¹¹ It is clearly seen that binary (Ni(II):Ade and Ni(II):Leu) and ternary (Ni(II):Ade:L-Leu) complex begin to form at the same time and at the same pH level (pH = 2.5). Moreover, Ni(II):Ade:L-Leu ternary complex is present as single dominant coordination species at pH = 6–10.

International Journal of Innovative Research in Science, Engineering and Technology

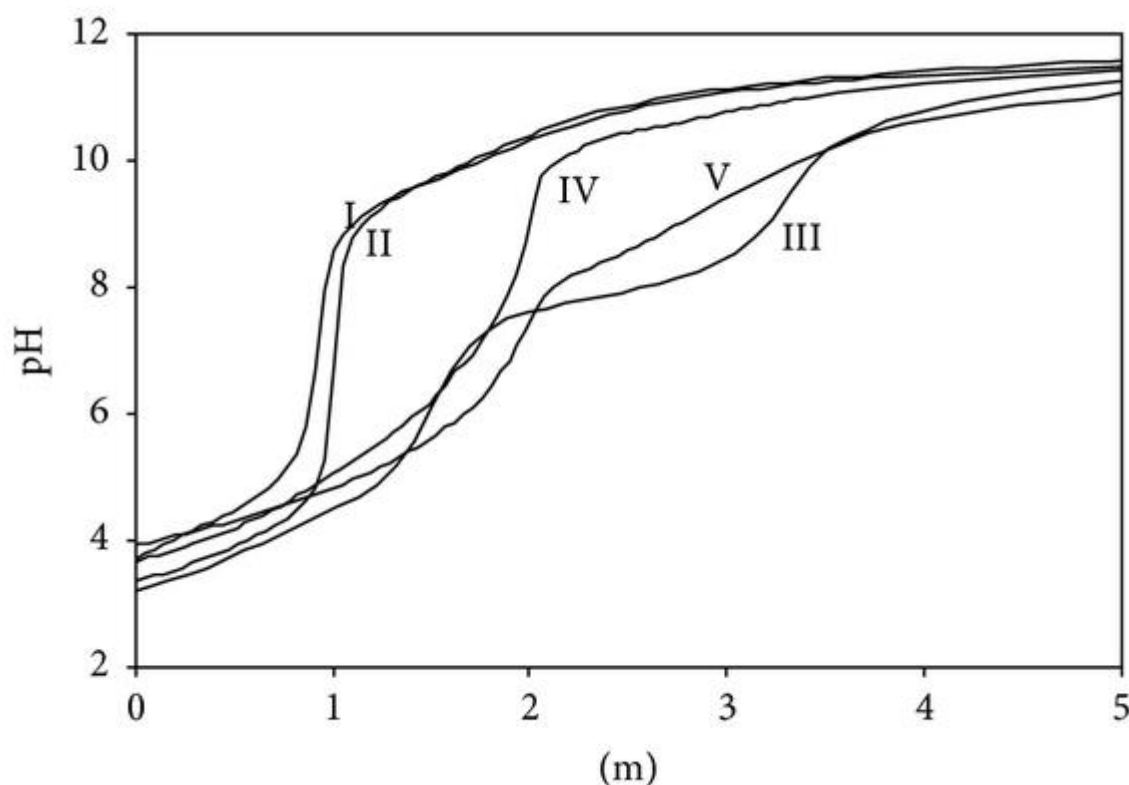
(A High Impact Factor, Monthly, Peer Reviewed Journal)

Visit: www.ijirset.com

Vol. 7, Issue 2, February 2018

Ni(II):Ade:L-Phe ternary complex formation also shows different trends from the other complexes of Ni(II) (Figure 9). Ni(II):L-Phe binary complex begins to form at pH = 2, and it reaches its maximum level (82%) at pH = 5. Ni(II):L-Phe binary complex begins to dissociate gradually at pH = 5, and it completely disappears at pH = 10. In this Ni(II), Ade, L-Phe mixture, Ni(II):Ade:L-Phe type ternary complex formation begins at pH = 4 and it reaches its maximum level at pH = 8.5.¹²

Unexpectedly, in Ni(II), Ade, L-Trp system, binary complex of Ni(II) is not detectable, since the Ni(II):Ade:L-Trp ternary complex dominates the reaction in this aqueous solution.¹² Formation of Ni(II):Ade:L-Trp ternary complex begins at pH = 3.8, and it reaches its maximum level at pH = 7.³⁰



II.DISCUSSION

The organometallic Ni(II) chemistry of the pyrrole-based pincer ligands, $(P_2^R\text{Pyr})^-$ ($P_2^R\text{Pyr} = 2,5-(R_2\text{PCH}_2)_2\text{C}_4\text{H}_2\text{N}$, R = Ph or Cy) is reported. Reactions of Grignard reagents with $[\text{NiCl}(P_2^R\text{Pyr})]$ afford a variety of alkyl and aryl complexes (methyl, ethyl, benzyl, phenyl, and allyl) that all display square planar geometries about nickel.¹³ The hydride complex, $[\text{NiH}(P_2^{\text{Cy}}\text{Pyr})]$, can also be prepared either through treatment of $[\text{NiCl}(P_2^{\text{Cy}}\text{Pyr})]$ with LiHBET_3 , or by reaction of $\text{H}(P_2^R\text{Pyr})$ with $[\text{Ni}(\text{COD})_2]$ (COD = 1,4-cyclooctadiene). Reactions of the methyl and hydride complexes with CO and CO_2 ,¹⁴ respectively, evince clean migratory insertion chemistry of the Ni-C and Ni-H bonds. Both the alkyl and chloride

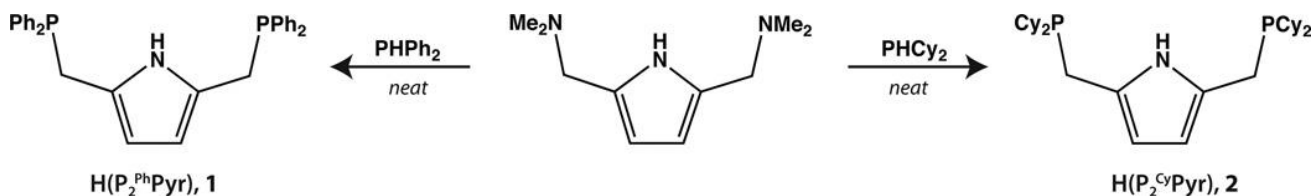
International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly, Peer Reviewed Journal)

Visit: www.ijirset.com

Vol. 7, Issue 2, February 2018

complexes are active catalysts for the Kumada coupling of aryl chlorides and aryl or alkyl Grignard reagents at room temperature. In this contribution, we extend the chemistry of the pyrrole-based PNP²⁹ ligand, P₂^{Ph}Pyr⁻, to a series of organometallic complexes of Ni(II). In addition, we report the synthesis and coordination chemistry of the new dicyclohexylphosphine-derived ligand, P₂^{Cy}Pyr⁻.¹⁵ This aliphatic pyrrole-diphosphine ligand is prepared in straightforward fashion and allows access to a variety of complexes not obtainable with the diphenylphosphine analog, P₂^{Ph}Pyr⁻. Nickel(II) complexes of both PNP ligands appear to be active catalysts for a variety of Kumada-type C-C cross coupling reactions.¹⁶



Scheme-1

Our initial synthesis of the pyrrole-diphosphine, H(P₂^{Ph}Pyr) (1),²⁸ involved reduction of the corresponding phosphine oxide to afford a BH³-protected precursor that was used directly in the synthesis of Ni(II) complexes. Concurrent reports by the groups of Gade and Mani demonstrated an alternative method for the preparation of 1 using the secondary phosphines¹⁶ (or potassium salts thereof) directly in displacement reactions with bis(aminomethyl)pyrrole precursors. We have adopted this synthetic methodology for the preparation of 1 and have extended it to include the formation of the dicyclohexylphosphine derivative (2) as shown in Scheme 1.²⁷ The formation of 2 from bis(dimethylaminomethyl)pyrrole occurs in higher yield than that for 1 presumably due to the increased nucleophilicity of the secondary alkyl phosphine. P NMR spectra of 2 display a single peak at -7.67 consistent with trivalent phosphorus. Similar to compound 1,¹⁷ no J_{HP} coupling is observed between the methylene protons of the pincer “arms” and the phosphorus nuclei by ¹H NMR spectroscopy. Thus far compound 2 has resisted efforts at crystallization and its sensitivity to air has hampered chromatographic purification. Fortunately, however, the preparation of compound 2 directly affords material of sufficient purity for attachment to nickel(II).¹⁸

III. RESULTS

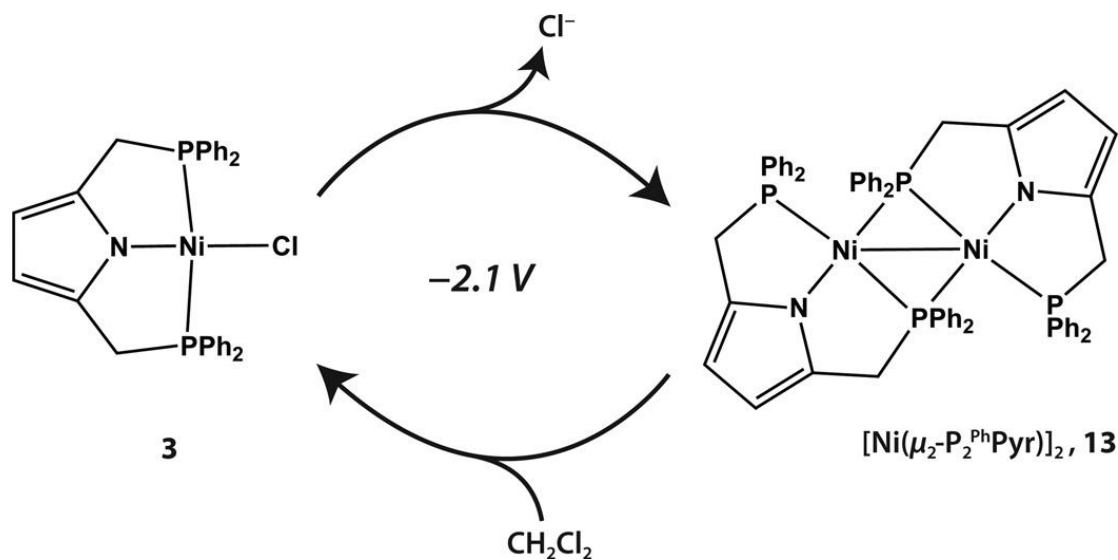
Previous electrochemical experiments with complex 3 demonstrated that an electrocatalytic process occurs in methylene chloride at low potentials.²⁶ This process most likely corresponds to the abstraction of a chlorine atom by the dimeric Ni(I) species, [Ni^I(μ₂-P₂^{Ph}Pyr)]₂ (13)¹⁹ which is formed by reduction of 3 around -2.1 V versus the ferrocene/ferrocenium couple (Scheme 2). To examine whether a similar process occurs for 4, its cyclic voltammogram was recorded in CH₂Cl₂.²⁵ In contrast to 3, the CV of 4 in CH₂Cl₂ displays no cathodic events within the solvent window. Such a result is consistent with the more reduced nature of 4 with respect to 3 due to the presence of the more electron-donating dicyclohexylphosphine groups of the ligand. In THF, the CV of 4 does display an irreversible cathodic event at low potentials.²⁰ Although not as well resolved as that observed for complex 3, the cathodic events are somewhat comparable.¹⁹ Whether this process corresponds to formation of an analogous Ni(I) dimeric species is not known at this time. However, treatment of 4 with hydride sources does not result in formation of an analogous Ni^I dimer as observed with 3.²¹

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly, Peer Reviewed Journal)

Visit: www.ijirset.com

Vol. 7, Issue 2, February 2018

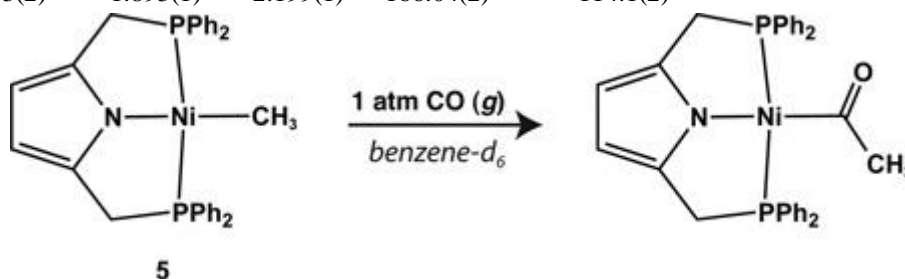


Scheme-2

IV. CONCLUSIONS

Selected bond distances (Å) and angles (deg) for nickel(II) hydrocarbyl complexes.²⁴

| Compound | Ni(1)-C(31) | Ni(1)-N(1) | Ni(1)-P _{avg} | P(1)-Ni(1)-P(2) | Ni(1)-C(31)-C(32) |
|----------------|-------------|------------|------------------------|-----------------|-------------------|
| 6 | 1.967(2) | 1.886(2) | 2.178(2) | 165.11(2) | N/A |
| 7 [†] | 1.997(2) | 1.891(2) | 2.182(1) | 166.60(3) | 111.4(1) |
| 10 | 1.980(1) | 1.890(1) | 2.198(1) | 158.83(2) | 110.9(1) |
| 11 | 1.903(1) | 1.884(1) | 2.179(1) | 167.57(1) | 122.3(1) |
| 14 | 1.993(2) | 1.893(1) | 2.199(1) | 166.04(2) | 114.1(2) |



Ni(NO₃)₂·6H₂O and diphenylamine formed a complex compound in 1:6 mole ratio of metal to ligand in methanol. The forming of the complex was indicated by shifting of maximum wavelength in UV-Vis spectra. Analysis of the nickel percentage in the complex by Atomic Absorption Spectroscopy (AAS) showed an empirical formula²² of the complex was Ni(diphenylamine)₄(NO₃)₂·6H₂O. The conductivity measurement of the complex showed the charge ratio of cation and anion = 1:1. It meant that NO₃⁻ was coordinated to the Ni²⁺ center ion and likewise as a counter ion. The

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly, Peer Reviewed Journal)

Visit: www.ijirset.com

Vol. 7, Issue 2, February 2018

formula of complex was approximated $[\text{Ni}(\text{diphenylamine})_4(\text{NO}_3)_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$. Based on infrared spectra, it revealed diphenylamine as monodentate ligand which bind to nickel(II) through the secondary NH functional groups. Electronic spectra showed a transition peak at 25252 cm^{-1} and 13802 cm^{-1} which indicating octahedral geometry. The complex was paramagnetic with $\mu_{\text{eff}} = 2.99\text{ BM}$.²³

REFERENCES

1. Singleton JT. Tetrahedron. 2003;59:1837–1857. [Google Scholar]
2. Morales-Morales D, Jensen CGM, editors. The Chemistry of Pincer Compounds. Amsterdam: Elsevier B. V; 2007. [Google Scholar]
3. van der Vlugt JJ, Reek JNH. Angew. Chem. Int. Ed. 2009;48:8832–8846. [PubMed] [Google Scholar]
4. Selander NJ, Szabó K. Chem. Rev. 2010;111:2048–2076. [PubMed] [Google Scholar]
5. van Koten G, Gebbink RJMK. Dalton Trans. 2011;40:8731–8732. [PubMed] [Google Scholar]
6. Gunanathan C, Milstein D. Acc. Chem. Res. 2011;44:588–602. [PubMed] [Google Scholar]
7. Haibach MC, Kundu S, Brookhart M, Goldman AS. Acc. Chem. Res. 2012;45:947–958. [PubMed] [Google Scholar]
8. Gelman D, Musa S. ACS Catal. 2012;2:2456–2466. [Google Scholar]
9. Vabre B, Canac Y, Duhayon C, Chauvin R, Zargarian D. Chem. Commun. 2012;48:10446–10448. [PubMed] [Google Scholar]
10. Benito-Garagorri D, Kirchner K. Acc. Chem. Res. 2008;41:201–213. [PubMed] [Google Scholar]
11. Castonguay A, Beauchamp AL, Zargarian D. Organometallics. 2008;27:5723–5732. [Google Scholar]
12. Leis W, Mayer HA, Kaska WC. Coord. Chem. Rev. 2008;252:1787–1797. [Google Scholar]
13. Castonguay A, Spasyuk DM, Madern N, Beauchamp AL, Zargarian D. Organometallics. 2009;28:2134–2141. [Google Scholar]
14. Schneider S, Meiners J, Askevold B. Eur. J. Inorg. Chem. 2012;2012:412–429. [Google Scholar]
15. He L-P, Chen T, Gong D, Lai Z, Huang K-W. Organometallics. 2012;31:5208–5211. [Google Scholar]
16. Wang Z-X, Liu N. Eur. J. Inorg. Chem. 2012;2012:901–911. [Google Scholar]
17. Hu X. Chem. Sci. 2011;2:1867–1886. [Google Scholar]
18. Chakraborty S, Zhang J, Patel YJ, Krause JA, Guan H. Inorg. Chem. 2012 [Google Scholar]
19. Grüger N, Wadepohl H, Gade LH. Dalton Trans. 2012;41:14028–14030. [PubMed] [Google Scholar]
20. Kumar S, Mani G, Mondal S, Chattaraj PK. Inorg. Chem. 2012;51:12527–12539. [PubMed] [Google Scholar]
21. Venkanna GT, Ramos TVM, Arman HD, Tonzetich ZJ. Inorg. Chem. 2012;51:12789–12795. [PubMed] [Google Scholar]
22. Hennessy ET, Betley TA. Science. 2013;340:591–595. [PubMed] [Google Scholar]
23. Mazet C, Gade LH. Organometallics. 2001;20:4144–4146. [Google Scholar]
24. Mazet C, Gade, Lutz H. Eur. J. Inorg. Chem. 2003;2003:1161–1168. [Google Scholar]
25. Li R, Larsen DS, Brooker S. New J. Chem. 2003;27:1353–1359. [Google Scholar]
26. Mashima K, Tsurugi H. J. Organomet. Chem. 2005;690:4414–4423. [Google Scholar]
27. Odom AL. Dalton Trans. 2005:225–233. [PubMed] [Google Scholar]
28. Lin C-Y, Tsai C-F, Chen H-J, Hung C-H, Yu R-C, Kuo P-C, Lee HM, Huang J-H. Chem.-Eur. J. 2006;12:3067–3073. [PubMed] [Google Scholar]
29. Tenza K, Hanton MJ, Slawin AMZ. Organometallics. 2009;28:4852–4867. [Google Scholar]
30. Hsu J-W, Lin Y-C, Hsiao C-S, Datta A, Lin C-H, Huang J-H, Tsai J-C, Hsu W-C. Dalton Trans. 2012 [PubMed] [Google Scholar]