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Synthesis And Investigation Of The Properties Of L-Tris (Parabenzylidene amino phenyl) Phosphite And Its Metal Carbonyl Derivatives

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ABSTRACT

The synthesis and investigation of the properties of the Schiff base tris(parabenzylideneaminophenyl)phosphite as well as the preparation in solution at atmospheric pressure (under N₂) of this compounds as a ligand (L) with some metal carbonyls (mononuclear) having the general formula shown below are described. $M(CO)_{n-x}L_x$, [M=Ni(0), n=4, x=1,2], [M=Fe(0), n=5, x=1], [M=Cr(0), n=6, x=1] L = (C₆H₅-CH=N-C₆H₄-O)₃P. Elemental analysis as well as infrared, ultraviolet-visible and NMR spectroscopic data are also presented.

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KEYWORDS

Carbonyl stability;
Chiral synthesis catalyst;
Spectroscopic
characterization.

INTRODUCTION

The preparation of L-tris(parabenzylideneaminophenyl) phosphate involving the reaction of parabenzylidene aminophenol with PCl₃ proceeds in refluxing 1,2-C₂H₄Cl₂ or toluene with the final product depending on the reaction conditions^[1]. During the reaction evolution of chlorine occurred and a yellow product was obtained. This new compound was postulated to be a potential substitute in the fabrication of certain types of rubbers, plastics and in particular, polyvinylchloride. Therefore this new synthetic moiety, [L = (C₆H₅-CH=N-C₆H₄-O)₃P], has the potential to be used in many practical applications as a replacement for a variety of materials^[2,3] that are currently in use. Another notable feature of this particular compound as a ligand is the stability of the carbon monoxide-metal bond. Such ligands could play an

important role in organometallic as well as coordination chemistry in general^[2,3]. Of particular importance is that phosphite ligands as part of a metal complex have been shown to have interesting chiral properties^[4,5] and have been used as effective catalysts in enantioselective synthetic processes^[6,7].

Ligands having electron-donating substituents are normally strong donors. Therefore, tertiary phosphine donates more strongly than tertiary phosphite to a metal, (electron effect and estimation of cone angle)^[8]. Coordination of the ligand to the metal, usually increases the electron density of the central metal atom, if only electron donation is considered. This observation apparently contradicts the electroneutrality principle of atoms in molecules when ligands coordinate to the electron-rich low valent metals. Typical examples are metal carbonyls in which the metal atom is frequently zero-valent.

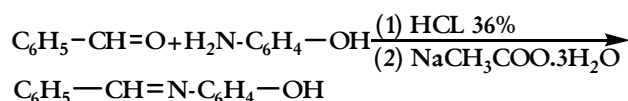
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When CO coordinates to a metal by its σ -HOMO at carbon, filled metal $d\pi$ orbitals of the transition metal will also overlap with the low lying π -LUMO of CO to give π -back-bonding interaction. This effect implies that CO not only donates two electrons by coordination, but also receives two electrons from the metal at the same time, thus stabilizing the M-CO bonds and weakening the $C\equiv O$ triple bond. In the case of phosphine compounds the σ^* and $3d$ orbitals are mixed^[8]. Therefore it is the mixture of orbitals which is the electron receiver. On the other hand, in phosphite compounds, π^* orbitals of aryl groups participate in receiving electron pairs from the nonbonding orbital of the central metal^[8]. The long-range electronic effects of phosphite ligands in certain metal complexes have already been documented^[9].

EXPERIMENTAL

Preparation of parabenzyldineaminophenol

26g(0.13mole) of paraaminophenol was added to HCl(11mL, 36%, 0.13mole). The mixture was stirred vigorously in an atmosphere of nitrogen at 25°C for 30mins, until a homogenous solution was obtained^[3,5]. Then, 19g of $NaOOC-CH_3 \cdot 3H_2O$ (0.135mole) was dissolved in 100mL of distilled water; this aqueous solution of acetate was slowly added to the above mixture. The solution was then stirred vigorously at room temperature resulting in a yellow viscous precipitate that was filtered and collected.

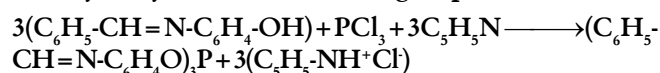


The residue was dissolved in a minimum amount of absolute ethanol, and then distilled. Water was added dropwise. A yellow brown residue was precipitated (parabenzyldine-aminophenol) and was washed on filter paper with methanol. The solid was dried under vacuum(m.p 178°C, yield 75%). The spectrum of this compound contained a sharp peak at 1660cm^{-1} showing the presence of the $>C=N$ group, and a broad peak at 3000cm^{-1} showing the existence of an OH group.

Synthesis of tris(parabenzyldine aminophenyl) phosphite

The best solvent for this synthesis was determined

to be 1,2 dichloroethane with the presence of a tertiary base (pyridine). Therefore, 8.8g (44.7mmol) of parabenzyldineaminophenol was dissolved in 60mL of 1,2-dichloroethane and 3.6mL of pyridine was added to the solution. The mixture was transferred to a 3-necked flask and 1.3ml of PCl_3 (14.9mmol) was added dropwise to the solution. The reaction was initiated under nitrogen at 55°C and then was refluxed at 90-95°C for 1hr. The mixture was then cooled to room temperature, filtered and the residue was washed several times thoroughly with water leading to the isolation of the pyridinium salt. There was no tertiary base hydrolyses of the $>C=N-$ group^[3,5,6].



The solvent was taken off in vacuum and the residue was dissolved in a minimum amount of 1,2-dichloroethane; then n-pentane was added dropwise to it. Tris(parabenzyldineaminophenyl) phosphite was the yellow product that was obtained. The final yield was 85%. The new compound started to become oily at a temperature of about 40-45°C and at a temperature of about 60-63°C became a clear liquid. The infrared spectrum of this compound in KBr is shown in TABLE 1.

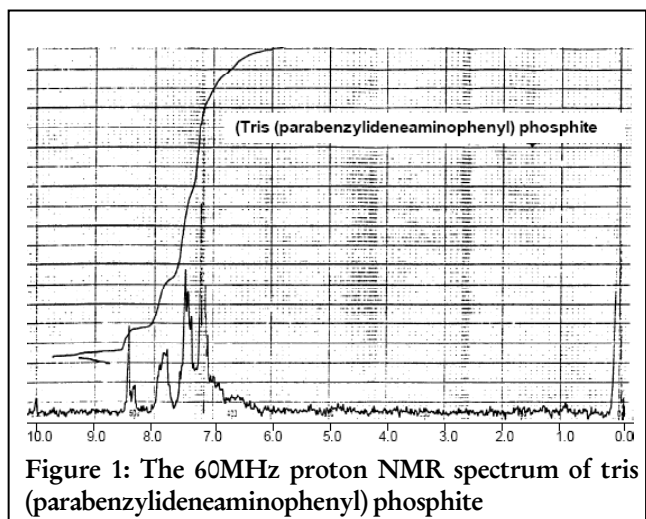
The NMR spectrum for the aromatic hydrogens (C-H) and the hydrogen in the $>C=N-H$ moiety is shown in figure 1. Analysis: Calculated for tris (parabenzyldineaminophenyl) phosphite) C, 75.59%; H, 4.85%; N, 6.70%. (Found: C, 75.51%; H, 5.1%; N, 6.65%)

Synthesis of tris (parabenzyldineaminophenyl) phosphitetriscarbonyl Ni(0)^[3,5,6]

1.85g of $(C_6H_5-CH=N-C_6H_4O)_3P$ (3mmol) was dissolved in 30ml of 1,2-dichloroethane and 0.14ml of $Ni(CO)_4$ (3mmole) was added to the solution. The mixture then was stirred in an atmosphere of nitrogen and refluxed for 4hr. The mixture was cooled to room temperature and filtered. The solution was removed under vacuum and the residue was redissolved in toluene for extraction of the ligand. The solution was then

TABLE 1

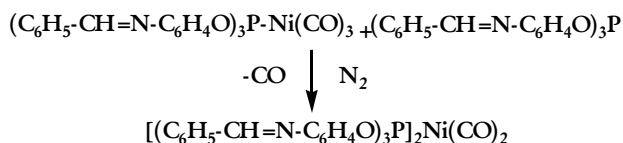
Imine	$>C=N-$	1622(cm^{-1})	Stretching frequency
Aromatic	C-H	3081(cm^{-1})	"
Aromatic	C=C	1500 (cm^{-1})	"
Aromatic	P-O-C	1185,1100,950(cm^{-1})	"



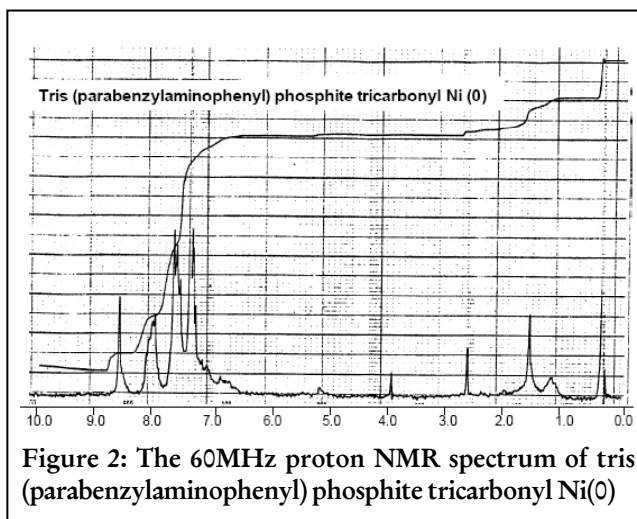
filtered under vacuum until a yellow precipitate was obtained. This product became oily at about a temperature of 45-50°C and at temperature of 65-70°C became a liquid. The infrared spectrum of this compound in KBr showed two bands in the carbonyl region; one relatively strong (E_1) at 2010 cm^{-1} and other of medium intensity (A_1) and sharp band at 2085 cm^{-1} . The IR spectrum of $\text{Ni}(\text{CO})_4$ contains one strong sharp^[7,8,9] band (T_2) at 2038 cm^{-1} . The NMR spectrum of this compound is shown in figure 2. Anal: The calculated composition for the proposed new compound is C, 66.20%; H, 3.94%; N, 5.50%; mol.wt: 765. (Found: C, 66.35%; H, 4.20%; N, 5.60%)

Synthesis of bis tris(parabenzylideneaminophenyl)phosphite]dicarbonyl Ni(0)^[3,5,6]

0.761g of the complex tris(parabenzylideneaminophenyl) phosphitetricarbonyl Ni(0), (1 mmol) was dissolved in 40ml of chloroform and 0.619g of the new ligand (phosphite), (1mmol) was added to it. The mixture was then vigorously stirred in an atmosphere of nitrogen at a temperature of about 55°C for 4hr.



The mixture was then cooled to room temperature and filtered. The solvent from the filtrate was removed under vacuum and the residue treated with 25mL of toluene in an atmosphere of N_2 at a temperature of 25°C for 90min, or until the excess of $\text{LNi}(\text{CO})_3$ was redissolved in toluene; the residue consisted of $\text{L}_2\text{Ni}(\text{CO})_2$ and unreacted ligand. This



precipitate was dissolved in a minimum amount of chloroform. In the latter solution, ethyl ether was added dropwise to 50% of the volume of CHCl_3 . Excess ligand remained in the solvent mixture and the residue was separated and isolated from the solution. This product became a clear liquid at a temperature of 45-50°C.

The infrared spectrum of this compound in KBr showed two bands in the carbonyl region. The new compound, $\text{L}_2\text{Ni}(\text{CO})_2$, has CO stretching frequencies in KBr at (A_1) 2040 cm^{-1} and (B_2) 1985 cm^{-1} . The NMR spectrum for this complex is shown in figure 3. Analysis: Calculated for this new compound is C, 70.95%; H, 4.43%; N, 6.20%. (Found: C, 71.15%; H, 4.45%; N, 6.10%)

Synthesis of [tris(parabenzylideneaminophenyl) phosphite] tetracarbonyl Fe(0)^[3,5,6]

0.42ml. of $\text{Fe}(\text{CO})_5$ (3mmole) was dissolved in 30ml of pure distilled toluene and 1.827g of $(\text{C}_6\text{H}_5\text{-CH=N-C}_6\text{H}_4\text{O})_3\text{P}$ was added to it (the ligand is insoluble in toluene). The mixture then was stirred in an atmosphere of N_2 in darkness at reflux temperature for 16hrs. This mixture was allowed to cool to room temperature and then filtered rapidly to separate the unreacted ligand. Next, the yellow-brown solution was immediately by vacuum. This process removed the solvent and unreacted $\text{Fe}(\text{CO})_5$. A dark brown residue was obtained, and this material was dissolved in pure distilled toluene. Then n-pentane was added dropwise. $\text{Fe}(\text{CO})_4\text{L}$ (brown) was precipitated and removed. Pentane was used for further washing and then the product was dried. This final

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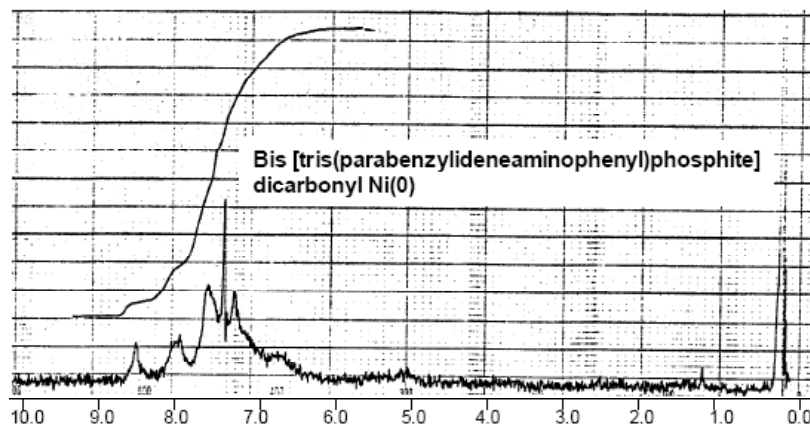


Figure 3 : The 60MHz proton NMR spectrum of bis [tris(parabenzylideneaminophenyl) phosphite]dicarbonyl Ni(0)

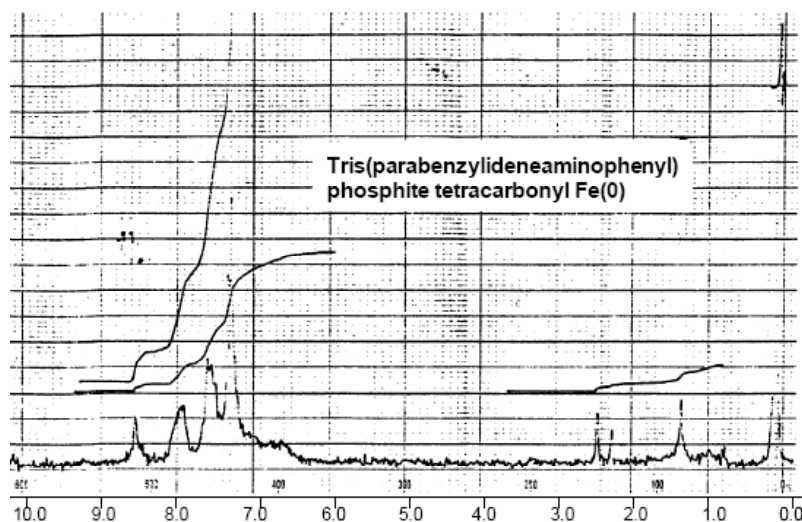


Figure 4 : The 60MHz proton NMR spectrum of tris(parabenzylideneaminophenyl) phosphite tetracarbonyl Fe(0)

product was a viscous liquid.

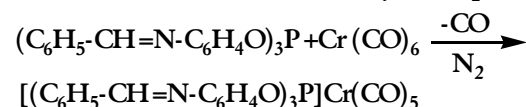
The infrared spectrum of this compound in KBr has three bands in the carbonyl region that are related to substitution in the axial position^[10]. $\text{LFe}(\text{CO})_4$ has CO stretching frequencies at (A_1) 2075cm^{-1} , (A_1) 1990cm^{-1} and (E) 1960cm^{-1} .

$\text{Fe}(\text{CO})_5$ has -CO stretching frequencies at (A'') 2028cm^{-1} and (E') 1994cm^{-1} . The NMR spectrum of this complex is shown in figure 4. Analysis: The calculated elemental analysis for this new compound is C, 65.56%; H, 3.90%; N, 5.30%. (Found: C, 65.84%; H, 4.10%; N, 5.45%) Attempts to obtain $\text{L}_2\text{Fe}(\text{CO})_3$ by this method were unsuccessful.

Synthesis of [tris(parabenzylideneaminophenyl) phosphite] pentacarbonyl Cr(0)

For preparation of this compound, a method simi-

lar to that of the iron carbonyl complex was used:



0.224g of $\text{Cr}(\text{CO})_6$ (1mmol) was dissolved in 25mL of pure toluene and 0.619g of tris (parabenzylideneaminophenyl)phosphite(1mmol) was added to the solution. The mixture then was stirred in an atmosphere of N_2 at reflux temperature for 14hrs. The mixture was then cooled to room temperature (25°C) and filtered. The solution was removed under vacuum at $60\text{-}65^\circ\text{C}$. The yellow residue started to become oily at a temperature of about 48°C , and at 65°C , it was a clear liquid.

The infrared spectrum of this compound in KBr has three bands in the carbonyl region. $\text{LCr}(\text{CO})_5$ has

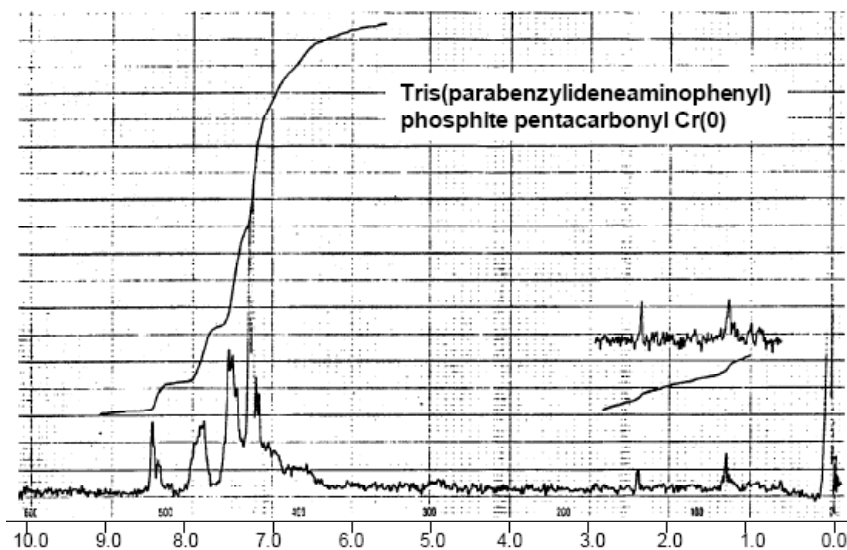


Figure 5 : The 60MHz proton NMR spectrum of tris(parabenzylideneaminophenyl) phosphite pentacarbonyl Cr(0)

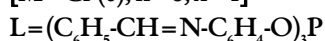
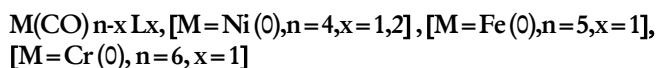
CO stretching frequencies at (A_1) 2080cm^{-1} , (A_1) 2000cm^{-1} and (E) 1960cm^{-1} . $\text{Cr}(\text{CO})_6$ has a single CO stretching band (T_{1u}) at 2000cm^{-1} [3,10]. The NMR spectrum of this species is shown in figure 5. Analysis: The calculated elemental analysis for this new compound is C, 65.10%; H, 3.69%; N, 5.18%. (Found: C, 65.30%; H, 3.80%; N, 5.30%). Attempts to obtain $\text{L}_2\text{Cr}(\text{CO})_4$ by this method were unsuccessful.

INSTRUMENTATION

Infrared spectra were obtained on a Perkin-Elmer (Norwalk, CT, USA) Model 595 spectrometer. The proton NMR spectra were acquired with a Hitachi Perkin-Elmer Model 435-1203 spectrometer in the continuous wave mode. Ultraviolet-visible spectra were obtained using a Milton Roy Model Spectronic 1201 (Rochester, NY) interfaced to a PC computer system.

RESULTS AND DISCUSSION

In this paper the phosphorous donor ligand tris(parabenzylideneamino-phenyl)phosphite has been synthesized. Then some organometallic derivatives of nickel tetracarbonyl, iron pentacarbonyl and chromium hexacarbonyl have been prepared with the general formula:



Ligands with electron-donating substituents are generally strong donors. Thus, tris(phenylphosphite) donates less strongly than tris(parabenzylideneaminophenyl) phosphite to metals. As a result, metal complexes with the new phosphite ligand ($\text{L}=(\text{C}_6\text{H}_5-\text{CH}=\text{N}-\text{C}_6\text{H}_4-\text{O})_3\text{P}$) are more electron-rich than the $(\text{C}_6\text{H}_5-\text{O})_3\text{P}$ analogues. Therefore such compounds are considered to be more susceptible to nucleophilic reactions and also to have stronger basicity.

Infrared studies of $\nu(\text{CO})$ for metal carbonyl derivatives often give valuable information about the structure and bonding of complexes with phosphite. The ligands are a weaker π -acceptor than the carbonyl group. Therefore, the CO stretching is shifted to a lower frequency. The infrared spectrum of the ligand (L) in KBr showed some bands in the $(\text{C}_6\text{H}_5-\text{C}=\text{N}-)$ region. The (A_1) stretching vibration in the metal carbonyl derivatives is a very important factor in determining the influence of basicity and reactivity of the ligand in this kind of organometallic compound[3]. A comparison of the $\nu(\text{CO})$ stretching frequencies of the derivatives of the different metal carbonyls of trisphenylphosphite with the new ligand (L) is shown in TABLE 2.

The benzylideneamino group ($\text{C}_6\text{H}_5-\text{C}=\text{N}-$) as an electron donor has influence on the electronic structure and basicity of ligand. Inductive and resonance effects act opposite to each other.

It appears that the resonance effects are slightly stronger than the inductive effects. Electronic effects

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TABLE 2 : Carbonyl stretching frequencies of the compounds in this study

L (Ligand)	LNi(CO) ₃		L ₂ Ni(CO) ₂	
	cm ⁻¹		cm ⁻¹	
	A ₁	E	A ₁	B
(PhO) ₃ P	2086.5	2018.5	2017	1999
(C ₆ H ₅ -CH=N-C ₆ H ₄ -O) ₃ P	2085	2015	2040	1990
L (Ligand)	LCr(CO) ₅ (cm ⁻¹)			
	A ₁	A ₁	E	
(PhO) ₃ P	2083	1975	1963	
(C ₆ H ₅ -CH=N-C ₆ H ₄ -O) ₃ P	2080	2000	1950	

in tertiary phosphine ligands have been estimated by using symmetrical stretching frequencies(A₁) of Ni(CO)₃PR₃ in CS₂^[5]. The following is the empirical equation for the trend:

$$\nu(\text{CO})(A_1) \stackrel{i=3}{\underset{i=1}{\equiv}} 2056.1 + \sum \chi_i (\text{cm}^{-1})$$

where χ_i denotes a substituent parameter of R on the P atom: χ_i for benzyldieneaminophenyl is described in the following equation^[11]:

$$(\text{KBr})2085(A_1) \stackrel{i=3}{\underset{i=1}{\equiv}} 2056.1 + \sum \chi_i (\text{cm}^{-1})$$

The UV spectra of the new compounds are as follows:

L	LNi(CO) ₃	L ₂ Ni(CO) ₂	LCr(CO) ₅
$\lambda_{\text{max}}(\text{nm})$	258	262	262

According to the UV spectra of these compounds, an increase in the λ_{max} (262nm) was noted in the singly substituted species^[12]. The value of λ_{max} is directly related to the transitions $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$. In the singly substituted complex, the ligand has strong σ -donor and weak π -acceptor back-bonding^[13]. Therefore, a pair of non-bonding electrons will move toward the aromatic ring. This action will increase the electron density at the nickel atom, which in turn decreases the energy level between π^* and n resulting in a shift to a longer λ_{max} (262nm)^[14].

In a doubly substituted complex the result is completely the opposite. The release of the 2nd CO group from the nickel carbonyl increases the electron density of nickel atom. This effect is due to an increase of the phosphite ligand's participation in the back-bonding of metal to ligand. As a result, the energy level between n and π^* will increase. This action results in a shift to a shorter λ_{max} (252nm) in comparison to the phosphite ligand itself with a λ_{max} of 258nm^[15].

In this new compound, the simultaneous existence of phosphite ester and imine functional groups

results in features such as the absorption of ultraviolet radiation in the 230-400nm range, an amorphous physical state, a moderate softening temperature and a resistance to hydrolysis which constitutes the bulk properties of the anti-oxidants. Accordingly, in view of these properties, it is anticipated that this new compound can be used as a substitute in rubbers, plastics and especially PVC functioning as an alternative in the formulation of these materials with a variety of potential applications^[16].

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