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Synthesis, Structure, and Hydrophosphorylation of π-Complexes Derived from *tert*-Butyl(1,3-dimethyl-2-butenylidene)amine and Homoligand Iron(0) and Group VIb Metal Carbonyls

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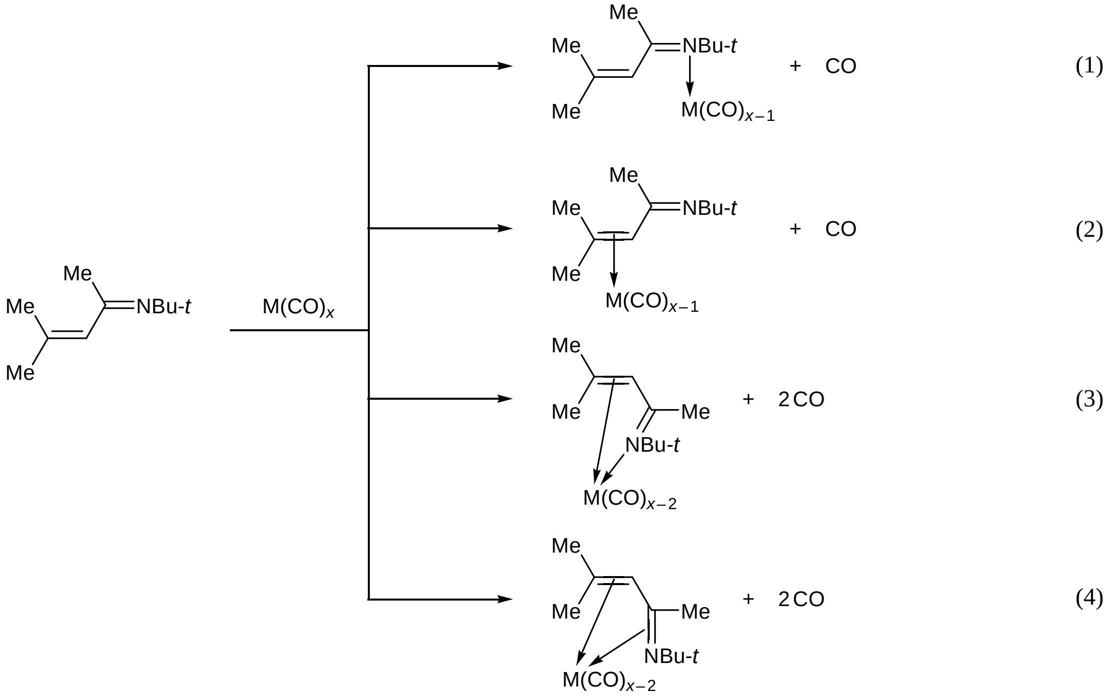
Abstract—New iron(0), chromium(0), molybdenum(0), and tungsten(0) π-complexes containing η^2-, η^3-, and η^4-coordinated *tert*-butyl(1,3-dimethyl-2-butenylidene)amine ligands were synthesized under conditions of photochemical and thermal activation. The geometric, electronic, and energetic parameters of the coordinated 1,3-azadiene were calculated by nonempirical methods, and factors determining the mode of coordination were established. The obtained π-complexes reacted with dialkyl phosphonates in the presence of triethylamine to afford organometallic α-aminophosphonates; hydrophosphorylation in the absence of a catalyst gave the corresponding amidophosphate which then underwent rearrangement into α-aminophosphonate.

We previously studied the reactivity of coordinated oxo diene systems, 1,3-diphenyl-2-propenone and benzylideneacetone, toward P–H-containing compounds [1, 2]. The results of these studies allowed us to develop a procedure for regioselective phosphorylation of the carbonyl group in the ligand coordinated to a transition metal. It should be emphasized that, regardless of the mode of coordination with metal, η^4 (at the C=C–C=O π-bond system) or η^2 (at the C=C bond), the phosphorus reagent adds exclusively at the heteroatom-containing double bond. We anticipated that analogous reaction with an azadiene ligand will give rise to a new method for inner-sphere synthesis of α-aminophosphonates which are known to possess practically useful properties [3]. The present article reports on the results of studying the synthesis of π-complexes derived from conjugated α,β-unsaturated Schiff bases and their phosphorylation with dialkyl phosphonates.

Azadiene systems containing conjugated C=C and C=N bonds are capable of coordinating to a metal center at both carbon–carbon and carbon–nitrogen π-bonds, as well as at lone electron pair on the nitrogen atom. In some cases, such compounds give rise to chelate structures [4]. As shown in [5, 6], nucleophilic addition of dialkyl phosphonates to enimines always occurs at the imine fragment. On the other hand, the diversity of ways for coordination of azadienes with metals implies the possibility for P–H reagent to react at any potential reaction center of the unsaturated ligand, namely C=C and C=N bonds and imino nitrogen atom. While predicting the probability for one or another synthetic result of inner-sphere hydrophosphorylation, one should also take into account essential reorganization of the steric and electronic structure of azadiene due to coordination [4].

With the goal of elucidating the preferential mode of coordination of *tert*-butyl(1,3-dimethyl-2-butenylidene)amine to pentacarbonyliron(0) and hexacarbonyl complexes of zero-valent metals of the chromium subgroup, we calculated the enthalpies of the corresponding reactions (1)–(4) (Scheme 1). The structural and energetic parameters were calculated in terms of the Hartree–Fock theory using the ECP (SBK) basis set where the inner-shell electrons are described by the Stevens–Bush–Krauss model potential. Hydrogen atoms were treated with the use of 6-31G basis set, and heavy-atom valence shells were described by the quadruple and triple zeta basis sets for *s*, *p*, and *d* shells, respectively; *d*-polarizing function was involved for heavy metal atoms. Using the above basis set, complete geometry optimization of the complexes was

Scheme 1.



M = Cr, Mo, W, x = 6; M = Fe, x = 5.

performed [7]. The applicability of this theoretical method for analysis of the structure and energy of formation of organometallic π-complexes was demonstrated by us previously [8].

While optimizing geometric parameters of the complexes derived from *tert*-butyl(1,3-dimethyl-2-butenylidene)amine, we considered four modes of coordination with metal carbonyl: (1) η^1: coordination at the lone electron pair (LEP) on the nitrogen atom; (2) η^2: metal coordination at the C=C bond; (3) η^3: bidentate coordination involving the C=C bond and lone electron pair on the nitrogen; and (4): η^4: diene coordination at the conjugated C=C–C=N π-bond system (Scheme 1).

Table 1. Calculated (RHF/SBK) enthalpies of reactions of *tert*-butyl(1,3-dimethyl-2-butenylidene)amine with carbonyl complexes of iron and chromium subgroup metals

Reaction no.	Δ*H*, kcal/mol			
	Cr	Mo	W	Fe
(1)	+0.7	+1.5	+1.6	–3.2
(2)	–11.0	–9.3	–6.1	–23.0
(3)	–24.2	–19.1	–16.2	–30.2
(4)	–15.6	–12.8	–10.3	–36.3

Table 1 contains the calculated enthalpies of reactions (1)–(4). It seen that the most energetically favorable for metals of the chromium soubgroup is formation of the complex η^3-(azadiene)M(CO)$_4$ and that the most stable iron carbonyl complex is η^4-(azadiene)Fe(CO)$_3$. Almost all complex formation reactions are characterized by exothermic effect due to higher strength of binding of the metal to *tert*-butyl-(1,3-dimethyl-2-butenylidene)amine rather than to carbon(II) oxide (Table 2). Exceptions are η^1-complexes formed via coordination at the nitrogen LEP. Thus the results of calculations suggest that, regardless of the metal nature, the most favorable process including replacement of one carbonyl ligand is reaction (2). The formation of η^3-complexes between the 1-aza-1,3-diene and metals of the chromium subgroup is preferred when two molecules of carbon(II) oxide are displaced from the metal coordination sphere. On the other hand, the reaction of pentacarbonyliron(0) with *tert*-butyl(1,3-dimethyl-2-butenylidene)amine, which is accompanied by replacement of two CO molecules, should give the corresponding η^4-complex.

The data in Table 3 show variations in the geometric and electronic structure of the *tert*-butyl(1,3-dimethyl-2-butenylidene)amine ligand as a result of coordination with metals, calculated for the corresponding π- and η,π-complexes. The most interesting is that η^3- or η^4-coordination of the azadiene changes the direction of polarization of the carbon–nitrogen bond in the ligand. In both cases, electron density transfer from the nitrogen atom to the metal leads to considerable increase of the negative charge on the imino carbon atom (the highest electron density in the free ligand is located on the nitrogen atom). For example, the charge on the C=N carbon atom in uncoordinated *tert*-butyl(1,3-dimethyl-2-butenylidene)amine is 0.008, and that on the nitrogen atom, –0.124. In the η^3-complex of *tert*-butyl(1,3-dimethyl-2-butenylidene)amine with tungsten carbonyl, the charges on the corresponding atoms are –0.102 and +0.123, respectively.

Coordination with metals leads to an appreciable extension of the C=C bond, which is observed for both η^2- and η^3-complexes with chromium subgroup metals and η^4-complex with iron. The C=N bond also becomes longer on complex formation, which is typical of organometallic compounds with increased order of π-coordination. These facts indicate rehybridization of coordination centers in the azadiene ligand and weakening of conjugation therein. The lengths of the multiple carbon–nitrogen and carbon–carbon bonds in the free ligand are 1.293 and 1.337 Å, respectively. In going to complexes with chromium, molybdenum, tungsten, and iron carbonyls, the lengths of the corresponding bonds become, respectively, 1.426 and 1.489, 1.432 and 1.495, 1.400 and 1.491, and 1.434 and 1.490 Å. Analysis of the data in Table 3 shows that the C=C–C=N fragment in the coordinated azadiene loses its planar structure: the torsion angle between the C=C and C=N bond planes varies from –35.8 to +67.1°, indicating considerable weakening of conjugation between these bonds.

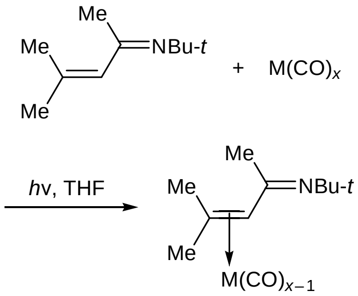
One more important parameter characterizing reduced conjugation in the C=C–C=N bond system is the energy of deformation [9, 10]. It ranges from 6 to 45 kcal/mol (Table 3) and increases in parallel with decrease in the electronegativity of the complex-forming metal. This may be interpreted in terms of increased electron density transfer from the metal to the olefin ligand in the π-complex. The energy of deformation calculated for the η^3- and η^4-complexes increases with rise in the atomic radius of the metal. Obviously, this is the result of essential structural rearrangement of the bidentate ligand, which becomes stronger as the size of atomic orbitals of the metal increases. Our further experiments confirmed the conclusions drawn on the basis of analysis of the results of quantum-chemical calculations.

Table 2. Calculated (RHF/SBK, additivity scheme) energies of dissociation (*D*) of M–L bonds in organometallic derivatives of *tert*-butyl(1,3-dimethyl-2-butenylidene)amine

Coordination mode	*D*(M–L), kcal/mol			
	Cr	Mo	W	Fe
η^1-N	40.6	35.7	37.2	45.4
η^2-C=C	62.3	46.5	45.3	65.2
η^2-C=C, η^2-C=N	98.2	87.2	88.7	120.7
η^2-C=C, η^1-N	106.8	93.5	94.6	114.6
(O≡C)–M	41.3	37.2	39.2	42.2

Photochemically activated reactions of *tert*-butyl (1,3-dimethyl-2-butenylidene)amine with transition metal carbonyls afforded compounds **Ia**–**Id** with the general formula η^2-[*tert*-butyl(1,3-dimethyl-2-butenylidene)amine]$M(CO)_{x-1}$, where x = 6 for chromium subgroup metals (M = Cr, Mo, W) and x = 5 for iron (M = Fe) (Scheme 2). In order to obtain just η^2-complexes, the syntheses of organometallic compounds were carried out with a considerable excess of the heterodiene to suppress haptotropic rearrangement of the latter [9].

Scheme 2.



Ia–**Id**

M = Fe (**a**), x = 5; Cr (**b**), Mo (**c**), W (**d**), x = 6.

The IR spectra of complexes **Ia**–**Id** contained an absorption band at 1580 cm^{-1} (1650 cm^{-1} in the spectrum of the free ligand), which was assigned to stretching vibrations of the coordinated C=C bond. The band at 1570 cm^{-1} (1575 cm^{-1} in the spectrum of the free azadiene) was attributed to vibrations of the uncoordinated C=N bond. In addition, five or four (for compound **Ia**) well resolved bands were present in the region 2000–1850 cm^{-1}; they correspond to coordinated carbon(II) oxide molecules. According to

Table 3. Calculated (RHF/SBK) interatomic distances, torsion angles $N^1C^2C^3C^4$ (φ), charges on the N^1 and C^2 atoms, and energy parameters of free and metal-coordinated *tert*-butyl(1,3-dimethyl-2-butenylidene)amine (L)

$t\text{-BuN}^1\text{=C}^2\text{(Me)–C}^3\text{H=C}^4\text{(Me}^5)_2$

Compound	Mulliken charges, $\bar{e}$		Bond length, Å			φ, deg	ΔΔ*H*,[a] kcal/mol	χ_M, eV, (R_M, Å)
	$q(N^1)$	$q(C^2)$	$N^1–C^2$	$C^2–C^3$	$C^3–C^4$			
L[b]	–0.124	+0.008	1.293	1.471	1.337	0	0	
$(\eta^2\text{-L})Cr(CO)_5$	–0.110	+0.014	1.288	1.526	1.472	–11.8	7.3	3.72
$(\eta^3\text{-L})Cr(CO)_4$	+0.075	–0.083	1.426	1.492	1.489	–6.2	24.6	(115.6)
$(\eta^4\text{-L})Cr(CO)_4$	+0.060	–0.033	1.383	1.511	1.507	+49	23.1	
$(\eta^2\text{-L})Mo(CO)_5$	–0.095	+0.021	1.289	1.509	1.492	–35.8	9.3	3.9
$(\eta^3\text{-L})Mo(CO)_4$	+0.123	–0.102	1.432	1.498	1.495	–5.11	30.9	(116.5)
$(\eta^4\text{-L})MoCO)_4$	+0.060	–0.033	1.376	1.501	1.495	+43.6	34.5	
$(\eta^2\text{-L})W(CO)_5$	–0.108	+0.044	1.288	1.507	1.491	+17.1	6.2	4.4
$(\eta^3\text{-L})W(CO)_4$	+0.123	–0.102	1.400	1.491	1.491	+67.1	44.8	(129)
$(\eta^4\text{-L})WCO)_4$	+0.060	–0.033	1.323	1.483	1.500	–47.1	33.1	
$(\eta^2\text{-L})Fe(CO)_4$	–0.128	+0.009	1.333	1.487	1.506	+24.6	28.2	4.06
$(\eta^3\text{-L})Fe(CO)_3$	+0.089	–0.102	1.434	1.492	1.490	–3.8	29.0	(130)
$(\eta^4\text{-L})Fe(CO)_3$	+0.102	–0.056	1.398	1.502	1.498	+18.5	36.4	

[a] According to Hoffmann [7, 8], the energy of ligand deformation (ΔΔ*H*) in the coordination sphere is defined as the difference between the enthalpy of formation of the ligand having a structure typical of organometallic compound and the enthalpy of formation of the uncoordinated ligand.

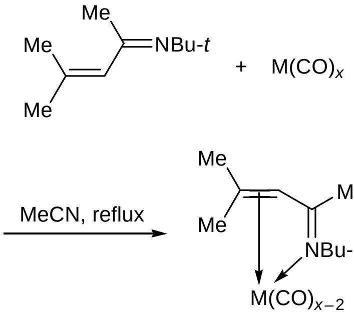
[b] L is *tert*-butyl(1,3-dimethyl-2-butenylidene)amine.

the ^{1}H NMR data, the complexes contain one molecule of the Schiff base which is coordinated to the metal via η^2-mode. In the ^{1}H NMR spectra of **Ia**–**Id**, signal from proton at the double bond appears at δ 4.2–4.7 ppm, while in the spectrum of the free ligand, the C=CH signal is located at δ 6.07 ppm (Table 4).

We believe that primary coordination of the azadiene to transition metal at the carbon–carbon π-bond is favored by the following. The formation of organometallic compounds from neutral metal complexes is orbital-controlled [10]; therefore, under conditions of kinetic control, the product should be a complex in which maximal overlap of the metal and ligand orbitals is achieved. In our case, the most favorable is overlap of the frontier orbital of the metal-containing fragment (which is a *d*-like orbital) with the symmetric frontier orbital of the Schiff base, which is localized on the C=C carbon atoms.

Under conditions of thermal activation, the resulting organometallic compounds are characterized by increased order of π-coordination. Here, the azadiene ligand replaces two carbon(II) oxide molecules. The coordination mode depends on the metal. Chromium metals give rise to η^3-[*tert*-butyl(1,3-dimethyl-2-butenylidene)amine]tetracarbonylmetal(0) complexes **IIa**–**IIc** where the ligand is coordinated with the metal through the carbon–carbon π-bond and nitrogen LEP (Scheme 3).

Scheme 3.



IIa–**IIc**

M = Cr (**a**), Mo (**b**), W (**c**); *x* = 6.

In the IR spectra of **IIa**–**IIc**, the band at 1580 cm^{-1} was assigned to stretching vibrations of the coordinated C=C bond. The C=N vibration frequency changes insignificantly (cf. 1565 cm^{-1} in the spectrum of **IIc** and 1575 cm^{-1} for the free ligand). Therefore,

Table 4. IR and ^{1}H NMR spectra of π-complexes derived from *tert*-butyl(1,3-dimethyl-2-butenylidene)amine and metal carbonyls

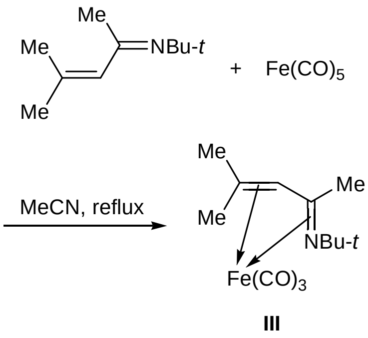
Compound no.	^{1}H NMR spectrum (DMSO-d_6), δ, ppm			IR spectrum, ν, cm^{-1}			
	C=CH	*t*-Bu	$(CH_3)_2C=$	C=C	C=N	CO in $M(CO)_x$	M–N
L[a]	6.05 br	0.33 s	2.82 s	1640	1570	–	–
Ia	4.34 br	0.35 s	2.65 s	1580	1570	2000, 1960, 1950, 1930, 1900	–
Ib	4.22 br	0.34 s	2.73 s	1580	1565	2010, 1980, 1970, 1920, 1880	–
Ic	4.44 br	0.35 s	2.72 s	1575	1560	2020, 1970, 1950, 1920, 1880	–
Id	4.52 br	0.33 s	2.66 s	1580	1570	2000, 1990, 1970, 1920, 1880	–
IIa	4.58 br	0.32 s	2.63 s	1590	1575	2010, 1980, 1880, 1840	840
IIb	4.62 br	0.27 s	2.70 s	1600	1575	2000, 1960, 1860, 1840	850
IIc	4.69 br	0.30 s	2.74 s	1610	1565	2000, 1960, 1880, 1840	870
III	4.22 br	0.29 s	2.68 s	1605	1510	1980, 1940, 1910	–

[a] L is *tert*-butyl(1,3-dimethyl-2-butenylidene)amine.

π-coordination at the C=N bond is lacking. In keeping with the data of [11], absorption bands in the region 870–880 cm^{-1} belong to vibrations of the nitrogen–metal dative bonds formed via donation of the nitrogen LEP to vacant *d* orbitals of the transition metal. Four absorption bands at 2000, 1960, 1880, and 1840 cm^{-1} correspond to the carbonyl ligands. In the ^{1}H NMR spectra of **IIa**–**IIc**, as well as of **Ia**–**Id**, signals from the olefinic proton are located at δ 4.2–4.7 ppm. The purity of complexes **IIa**–**IIc** was checked by thin-layer chromatography. The complexes melt within a narrow temperature range, and their IR spectra show no absorption at 1800 cm^{-1} [C=O stretching vibrations in bridging carbon(II) oxide ligands]. These data indicate that the nuclearity of complexes **IIa**–**IIc** is the same as of initial metal carbonyls, i.e., they are mononuclear complexes with the composition (azadiene)$M(CO)_4$.

Thermal reaction of *tert*-butyl(1,3-dimethyl-2-butenylidene)amine with pentacarbonyliron(0) afforded complex **III** with the composition (azadiene)$Fe(CO)_3$ (Scheme 4). It was formed by replacement of two carbon(II) oxide ligands in the initial iron(0) complex.

Scheme 4.



Unlike complexes **IIa**–**IIc**, iron(0) π-complex **III** is characterized by a different mode of coordination of the Schiff base to the metal [12, 13]. η^4-Coordination of the azadiene at the C=C–C=N π-bond system was confirmed by spectral data. Insofar as the imine fragment of the ligand is involved in coordination, the C=C stretching vibration frequency is reduced to 1610 cm^{-1}. The band at 1510 cm^{-1} was assigned to vibrations of the coordinated C=N bond. Three carbonyl ligands at the iron atom give rise to three absorption bands at 1980, 1940, and 1910 cm^{-1}. On the other hand, the IR spectrum contains no bands assignable to vibrations of dative nitrogen–metal bonds.

In the ^{13}C NMR spectrum of **III**, signals from carbon atoms in the η^4-coordinated azadiene ligand are observed in an appreciably stronger field, as compared to the free ligand. This fact provides an additional support to the assumed coordination mode. The ^{13}C NMR spectrum of uncoordinated *tert*-butyl(1,3-dimethyl-2-butenylidene)amine contains signals at δ_C 147 (**C**=CH), 127 (C=**C**H), and 165 ppm (**C**=N); the corresponding signals in the spectrum of **III** are located at δ_C 63, 51, and 86 ppm, respectively. Thus, both IR and NMR data clearly indicate that the heterodiene ligand is coordinated to the metal through both C=C and C=N double bonds, giving rise to η^4-(heterodiene)$Fe(CO)_3$ complex.

Our results revealed that the mode of coordination of the azadiene depends on the metal nature. Analogous examples were described in [14–16] where complex formation of Schiff bases with iron and chromium subgroup metals was studied.

In continuation of our studies on phosphorylation of azadienes coordinated to transition metals, we examined reactions of compounds **IIa**–**IIc** with diethyl phosphonate. By analogy with oxo dienes [1, 2], we expected that coordinated enimines will take up dialkyl phosphonates at the most electrophilic C=N bond to give the corresponding α-aminophosphonates with retention of η^2-coordination at the C=C bond. On the other hand, taking into account high strength of the nitrogen–metal dative bond, we cannot rule out the possibility for hydrophosphorylation to occur at the olefinic fragment due to specific blocking of the nitrogen atom or C=N bond by the metal. It should be noted that hydrophosphorylation of uncoordinated unsaturated Schiff bases is strictly regioselective: it follows the Pudovik reaction scheme with participation of the C=C bond [3].

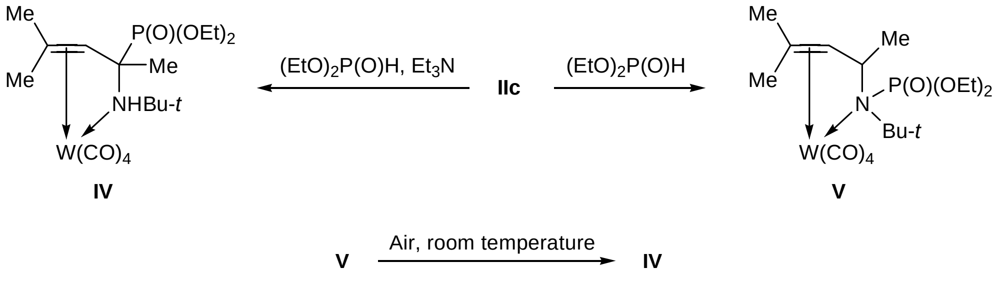
Diethyl phosphonate reacted with complex **IIc** both in the presence of a base catalyst and in the absence of it. The reaction catalyzed by triethylamine afforded α-aminophosphonate **IV** (Scheme 5) whose structure was determined on the basis of its ^{31}P NMR and IR spectra. In keeping with the data of [3], the singlet in the ^{31}P NMR spectrum at δ_P 14.8 ppm was assigned to the aminophosphonate structure. After partial removal of the solvent, the IR spectrum of the reaction mixture indicated the presence in molecule **IV** of an NH group (3200 cm^{-1}), double C=C bond coordinated to metal (1560 cm^{-1}), and carbonyl ligands (a complex set of bands). Also, an absorption band at 875 cm^{-1} was observed, which was assigned to the N–W bond.

Hydrophosphorylation in the absence of base catalyst was characterized by a different regioselectivity: the addition product was coordinated amidophosphate **V** (Scheme 5). Its ^{31}P NMR spectrum contained a signal at δ_P 7.3 ppm with satellites due to coupling with tungsten, $^1J(^{31}\text{P}–^{183}\text{W})$ = 185 Hz, which corresponds to indirect magnetic interaction between the ^{183}W and ^{31}P nuclei. According to the IR data, complex **V** has no N–H bond but contains nitrogen–tungsten dative bond (870 cm^{-1}) and metal-coordinated C=C bond (1570 cm^{-1}). On prolonged exposure to air at room temperature, amidophosphate **V** undergoes rearrangement into aminophosphonate **IV**.

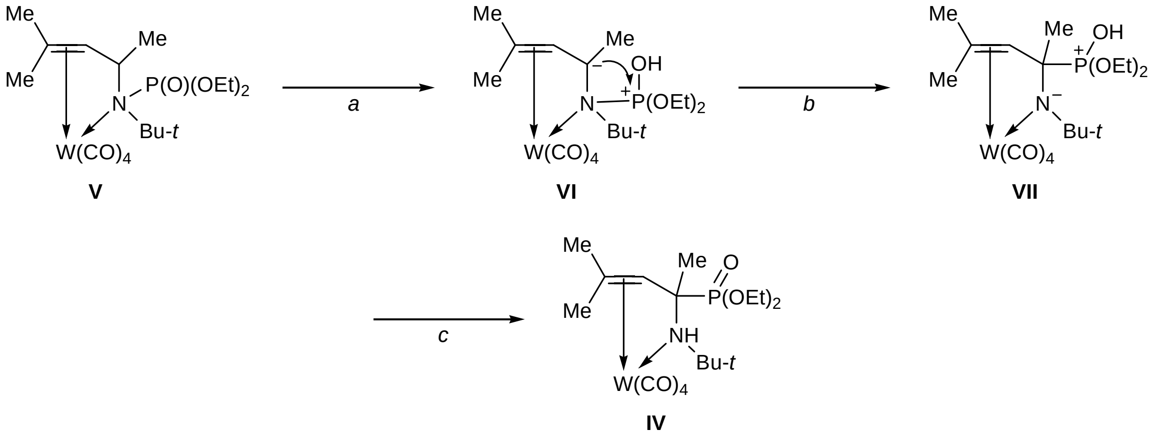
Our previous studies on inner-sphere phosphorylation of conjugated C=C–C=O systems [1, 2] also showed that P–H reagents add exclusively at the carbonyl group of oxo diene. The formation of phosphorylation products at the C=N bond of the C=C–C=N system may be explained by weakening of conjugation between the C=C and C=N bonds as a result of coordination to metal center. This leads to increase in electrophilicity of the carbon–heteroelement bond, which makes it the most susceptible to nucleophilic attack by phosphorus-containing reagent. Moreover, stronger bonding of the metal to the C=C bond rather than to C=N (Table 2) hampers addition at the former.

The formation of amidophosphate **V** in the absence of catalyst may be explained on the assumption that η^3-coordination of *tert*-butyl(1,3-dimethyl-2-butenylidene)amine with the metal changes polarization of the C=N bond (Table 3); as a result, the nitrogen atom becomes the most electrophilic. As far as we know, the formation of amidophosphates in phosphorylation of Schiff bases is an exception rather than a rule [17]. The subsequent rearrangement of amidophosphate **V** into aminophosphonate **IV** is favored by the greater thermodynamic stability of the latter. RHF/SBK quantum-chemical calculations of structures **V** and **IV** showed that the isomerization **V** → **IV** is exothermic; the enthalpy of the reaction is –3.7 kcal/mol. The mechanism of the observed inner-sphere amidophosphate–aminophosphonate rearrangement is likely to involve initial proton transfer from the α-carbon atom to the basic oxygen atom of the phosphinoyl group (step *a* in Scheme 6)) to give hydroxyphosphonium intermediate **VI**. This step is followed by attack by carbanion on the positively charged phosphorus atom (step *b*). The isomerization process is completed by

Scheme 5.



Scheme 6.



prototropic rearrangement **VII** → **IV** (step *c*). Analysis of the proposed mechanism in terms of the RHF/SBK procedure gives a relatively low activation barrier to step *a* (E_a = 9.7 kcal/mol). It is well known that hydrogen atom at a carbon atom in the α-position with respect to a phosphinoyl group is characterized by increased acidity (see [18] and references therein); in our case, this is supplemented by stabilizing effect of the electron-acceptor vinyl group coordinated to metal carbonyl on the carbanionic center emerging as a result of prototropic rearrangement (step *a*). Presumably, the presence of triethylamine favors formation of α-aminophosphonate **IV** by accelerating both formation of the kinetically controlled product, amidophosphate **V**, and proton transfer processes. Therefore, we observe formation of the thermodynamically controlled product, aminophosphonate **IV** while its precursor **V** is not detected.

Another possible reason for formation of α-aminophosphonate **IV** in the base-catalyzed hydrophosphorylation of complex **IIc** is that triethylamine coordinates to the metal, thus displacing the imino nitrogen atom from the coordination sphere of transition metal [15]. The resulting complex is like η^2-[(C=C)azadiene]tetracarbonyl(triethylamine)metal(0) in which the C=N bond is sensitive to nucleophilic attack. Naturally, the character of electron density distribution in the ligand almost does not differ from that typical of uncoordinated 1-aza-1,3-diene, and attack by organophosphorus nucleophile on the electrophilic carbon atom of the C=N bond occurs according to the imino version of the Pudovik reaction. We did not examine phosphorylation in the presence of other base catalysts, for they destroy the organometallic substrate [19].

Unfortunately, our numerous attempts to isolate phosphorylated complexes **IV** and **V** were unsuccessful; possible reasons are reversibility of the hydrophosphorylation process [3] and side reactions involving oxidation or hydrolysis of the complex during its isolation.

Our results demonstrate the possibility for controlling regioselectivity in the hydrophosphorylation of unsaturated Schiff bases and extending the synthetic potential of the Pudovik reaction by variation of intramolecular electronic interactions in unsaturated systems as a result of coordination with transition metals.

EXPERIMENTAL

The IR spectra were obtained on a Specord M-80 spectrometer from samples dispersed in mineral oil. The ^{1}H NMR spectra were recorded on Varian Unity 300 (299.94 MHz), Bruker 100 (100 MHz), and Brucker Gemini 200 instruments (199.827 MHz) at 25°C using benzene-d_6, chloroform-*d*, and methanol-d_4 as solvents (c = 0.7–1.5 wt %; the chemical shifts were measured relative to signals from residual protons in the solvent. The ^{13}C NMR spectra were recorded on a Varian Unity 300 spectrometer (75.4 MHz); the chemical shifts were measured relative to the signal of chloroform-*d*. TLC analysis was performed on Silufol plates using isopropyl alcohol–benzene (3:1, by volume) as eluent; the chromatograms were developed with iodine vapor. All experiments were carried out under argon.

Quantum-chemical calculations were performed using GAMESS 98 software [7]. The structural and energetic parameters of the compounds under study were calculated using the ESR (SBK) basis set where inner-shell electrons are described by a model potential.

η^2-[*tert*-Butyl(1,3-dimethyl-2-butenylidene)amine]pentacarbonyltungsten(0) (Id). A glass flask equipped with a balloon for supplying argon and a glycerol seal was charged with 0.20 g of *tert*-butyl-(1,3-dimethyl-2-butenylidene)amine and 15 ml of tetrahydrofuran. Hexacarbonyltungsten(0), 0.69 g, was added, and the mixture was irradiated for 2 h with UV light generated by a high-pressure mercury lamp. A crystalline solid precipitated from the mixture. When the reaction was complete, the product (yellow crystals) was filtered off and reprecipitated from benzene with pentane. Yield 0.22 g (30%), mp 145–150°C (decomp.). IR spectrum, ν, cm^{-1}: 1580 (C=C, coordinated); 1570 (C=N, uncoordinated); 2000, 1990, 1970, 1920, 1880 [CO in $W(CO)_5$]. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 4.52 br (C=CH).

η^2-[*tert*-Butyl(1,3-dimethyl-2-butenylidene)amine]-tetracarbonyliron(0) (**Ia**), η^2-[*tert*-butyl(1,3-dimethyl-2-butenylidene)amine]pentacarbonylchromium(0) (**Ib**), and η^2-[*tert*-butyl(1,3-dimethyl-2-butenylidene)-amine]pentacarbonylmolybdenum(0) (**Ic**) were synthesized in a similar way (Table 4).

η^3-[*tert*-Butyl(1,3-dimethyl-2-butenylidene)amine]tetracarbonyltungsten(0) (IIc). A mixture of 0.40 g of hexacarbonyltungsten(0) and 20 ml of dry degassed acetonitrile was heated for 40 min at the boiling point under argon, 0.250 g of *tert*-butyl(1,3-dimethyl-2-butenylidene)amine was added, and the mixture was heated for 14 h under reflux. Most part of the solvent was distilled off under reduced pressure (water-jet pump) without heating. The yellow crystalline material was filtered off under argon and reprecipitated from benzene with pentane. Yield 40%, yellowish finely crystalline powder, mp 76–80°C (decomp.). IR spectrum, ν, cm^{-1}: 1610 (C=C, coordinated); 1565 (C=N, uncoordinated); 2000, 1960, 1880, 1840 [CO in $W(CO)_4$]; 940 (W–N). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 4.69 br (C=CH).

η^3-[*tert*-Butyl(1,3-dimethyl-2-butenylidene)amine]-tetracarbonylchromium(0) (**IIa**) and η^3-[*tert*-butyl(1,3-dimethyl-2-butenylidene)amine]pentacarbonylmolybdenum(0) (**IIb**) were synthesized in a similar way (Table 4).

η^4-[*tert*-Butyl(1,3-dimethyl-2-butenylidene)amine]tricarbonyliron(0) (III). A mixture of 0.400 g of pentacarbonyliron(0) in 20 ml of dry degassed acetonitrile was heated for 40 min at the boiling point under argon, 0.250 g of *tert*-butyl(1,3-dimethyl-2-butenylidene)amine was added, and the mixture was heated for 14 h under reflux. Most part of the solvent was distilled off under reduced pressure (water-jet pump) without heating. The yellowish crystalline material was filtered off under argon and reprecipitated from benzene with pentane. Yield 27%, light orange finely crystalline powder, mp 83–87°C (decomp.). IR spectrum, ν, cm^{-1}: 1605 (C=C, coordinated); 1510 (C=N, coordinated); 1980, 1940, 1910 [CO in $Fe(CO)_3$]. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 4.22 br (C=CH).

Reaction of η^3-[*tert*-butyl(1,3-dimethyl-2-butenylidene)amine]tetracarbonyltungsten(0) with diethyl phosphonate in the presence of triethylamine. A 0.15-g (0.33-mmol) portion of η^3-[*tert*-butyl-(1,3-dimethyl-2-butenylidene)amine]tetracarbonyltungsten(0) was dissolved in 5 ml of dry degassed benzene, 0.2 ml of diethyl phosphonate, and 1–2 drops of triethylamine were added, and the mixture was kept for 24 h at room temperature under argon. The solvent was distilled off under reduced pressure (water-jet pump) to obtain a viscous amorphous material. The conversion of diethyl phosphonate into α-aminophosphonate **IV** was 85% (according to the ^{31}P NMR spectrum of the reaction mixture). IR spectrum, ν, cm^{-1}: 1560 (C=C, coordinated), 3200 br (N–H), 1900–2000 (CO, unresolved bands). ^{31}P NMR spectrum (reaction mixture): δ_P 14.8 ppm.

Reaction of η^3-[*tert*-butyl(1,3-dimethyl-2-butenylidene)amine]tetracarbonyltungsten(0) with diethyl phosphonate in the absence of triethylamine. The procedure was the same as above with the difference that no triethylamine was added. According to the ^{31}P NMR data, the conversion of diethyl phosphonate into amidophosphate **V** was 90%. IR spectrum, ν, cm^{-1}: 1560 (C=C, coordinated), 960 (N–W), 1900–2000 (CO, unresolved bands). ^{31}P NMR spectrum (reaction mixture): δ_P 7.3 ppm, $J(^{31}P–^{183}W)$ = 185 Hz. After 7 days at room temperature, the signal at δ_P 7.3 ppm disappeared from the spectrum, while that located at δ_P 14.8 ppm appeared with the same intensity.

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