Organometallics 1991, 10, 1527-1530

complexes 2 and 14 (which could result from either competitive PMe_3 dissociation from $Cp^*Re(CO)_2(PMe_3)$ or PMe_3 loss from 12 during photolysis). No product of C–H oxidative addition of propene to the intermediate $Cp^*Re(CO)(PMe_3)$ was observed.

While complex 12 seems to be reasonably stable under irradiation (above), minor amounts of the same products are formed in the irradiation of 12 alone, as are formed when $Cp^*Re(CO)(PMe_3)(L)$ (L = CO, N_2) are irradiated in the presence of propene. Interestingly, we saw no NMR evidence for the new allyl hydrido complex $Cp^*Re(PMe_3)(H)(\eta^3\text{-}C_3H_5)$ that might arise from CO loss from 12 followed by propene activation, in parallel with the results for 2.

Conclusions

The photolysis of $(C_5Me_5)Re(CO)_3$ in the presence of a variety of alkenes is similar to previously reported photolyses of the manganese complexes $(C_5H_5)Mn(CO)_3$, $(C_5H_4Me)Mn(CO)_3$, and $(C_5Me_5)Mn(CO)_3$[5,7,20] in providing analogous rhenium alkene complexes of the type $(C_5Me_5)Re(CO)_2(\eta^2\text{-alkene})$. However, a major difference is that on continued photolysis of the rhenium alkene complexes, intramolecular C–H activation occurs. The propene complex 2 has been studied in most detail, and the exo and endo isomers of the product allyl hydrido complex 14 have been fully characterized. Continued photolysis of the cyclohexene complex 6 yielded evidence for dehydrogenation products. These results further establish that organometallic compounds of rhenium are capable of entering into carbon–hydrogen activation reactions,[30,31,55] and work in this area is continuing.

Acknowledgment. This work was supported by NSERC Canada through an operating grant.

Supplementary Material Available: Textual details of the mass spectra of complexes 1–17 and the assignment of the ^1H NMR spectra of *exo*-14 and *endo*-14 and mass spectra for complexes 1–17 (8 pages). Ordering information is given on any current masthead page.

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Ketene Reactivity of *trans*-Bis(tricyclohexylphosphine)(η^1-formylketenyl)hydridoplatinum(II). Crystal and Molecular Structure of the Aniline Derivative. 17[1]

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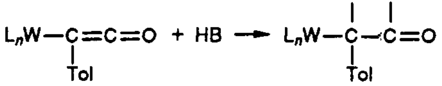
Received August 16, 1990

The (η^1-formylketenyl)platinum(II) complex $(PCy_3)_2Pt(H)(\eta^1\text{-}C(CHO)CO)$ reacts with primary aliphatic or aromatic amines, yielding the addition products $(PCy_3)_2Pt(H)C[(CHOH)(C(O)NHR)]$. The crystal structure of the aniline derivative has been determined. The crystals are monoclinic, $P2_1/c$, with a = 20.883 (12), b = 12.017 (6), c = 18.490 (8) Å, β = 108.00 (6)°, Z = 4. The amine adds to the C=O bond of the ketenyl group forming a planar ligand orthogonal to the coordination plane of Pt.

Introduction

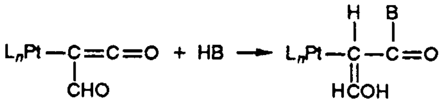
Recently there has been widespread interest in synthesis and reactivity studies on η^1-ketenyl complexes as synthons in addition reactions in organic chemistry. A simple synthetic route to obtain these complexes proceeds via insertion of carbon suboxide, C_3O_2, into metallic hydride bonds.[2] In the course of our systematic research on the reactivity of C_3O_2 we have obtained *trans*-$L_2Pt(H)(\eta^1\text{-}C(CHO)CO)$ by reacting C_3O_2 with *trans*-L_2PtH_2, with L = PCy_3, $Pi\text{-}Pr_3$.[3]

Scheme I



$$L_nW{-}\underset{\text{Tol}}{\underset{|}{C}}{=}C{=}O + HB \longrightarrow L_nW{-}\overset{H}{\overset{|}{\underset{\text{Tol}}{\underset{|}{C}}}}{-}\overset{B}{\overset{|}{C}}{=}O$$

Scheme II



$$L_nPt{-}\underset{\text{CHO}}{\underset{|}{C}}{=}C{=}O + HB \longrightarrow L_nPt{-}\overset{H}{\overset{|}{\underset{\text{HCOH}}{\underset{\|}{C}}}}{-}\overset{B}{\overset{|}{C}}{=}O$$

A full appreciation of the value of these compounds requires understanding of their structures, preferred conformations and mechanisms of reaction.[4] Actually, η^1-

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(1) Part 16: Ganis, P.; Paiaro, G.; Pandolfo, L.; Valle, G. *Gazz. Chim. Ital.* **1990**, *120*, 541.

(2) Hillhouse, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 7772.

(3) Pandolfo, L.; Paiaro, G. *Gazz. Chim. Ital.* **1990**, *120*, 531.

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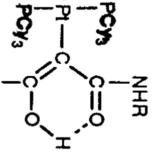
ketenyl complexes have been described to behave as ketenes themselves[5] and react with nucleophilic compounds, such as HB, for instance, according to Scheme I, where the addition involves the β-carbon atom.

In contrast with these findings we have observed that η^1-ketenyl Pt complexes react by a completely different mechanism (Scheme II).

When the addition reaction takes place between *trans*-bis(tricyclohexylphosphine)(η^1-formylketenyl)hydridoplatinum(II) (1)[3] and primary amines we obtain



2

Here we report a study on this reaction, physicochemical data for the reaction product 2 and the X-ray crystal analysis of the aniline derivative.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of argon in oven-dried glassware. Solvents were purified, dried, and distilled before use. 1 was prepared as previously reported.[3] Amines (aniline, *p*-nitroaniline, *tert*-butylamine, *n*-propylamine) were purified by distillation or crystallization before use. Infrared spectra were obtained on a Perkin-Elmer 597 spectrophotometer. ^{1}H and ^{31}P NMR spectra were recorded on a Varian EM 360 A or a Bruker AM 400 instrument. Elemental analyses were provided by the Microanalysis Laboratory of the CIMA Department of the University of Padova.

Synthesis of $(PCy_3)_2(H)PtC[(CHOH)(C(O)NHR)]$ (2) [R = Ph (a), *p*-$NO_2C_6H_4$ (b), *t*-Bu (c), *n*-Pr (d)]. The syntheses of 2a–d were performed by reacting equimolecular amounts of 1 and amine, both dissolved in benzene. A typical synthesis of 2a was carried out as follows: 1 (0.450 g, 0.54 mmol) was dissolved in 50 mL of C_6H_6. At room temperature 0.051 g of $C_6H_5NH_2$ (0.54 mmol) was added and the solution was stirred for 30 min. The solution was evaporated under vacuum and the residual solid compound was recrystallized from toluene/*n*-hexane, giving 0.290 g of white crystals of 2a (yield 58%).

2a: Mp 194–197 °C. IR (C_6H_6): ν(NH) 3275, ν(PtH) 2000, ν(CO) 1587 cm^{-1}; ^{31}P NMR (C_6D_6, 28 °C, δ): 33.32 (t), $J(^{195}Pt-^{31}P)$ = 2695 Hz. Anal. Calcd for $PtC_{45}H_{75}NO_2P_2$: C, 58.78; H, 8.23; N, 1.52. Found: C, 59.02; H, 8.10; N, 1.45.

2b: Recrystallized from toluene. Yield 52%. Mp: 198–202 °C. IR (C_6H_6): ν(NH) 3270, ν(PtH) 2010, ν(CO) 1608 cm^{-1}. Anal. Calcd for $PtC_{45}H_{74}N_3O_4P_2$: C, 56.06; H, 7.74; N, 2.91. Found: C, 56.52; H, 7.78; N, 2.81.

2c: Recrystallized from toluene/*n*-hexane. Yield 42%. Mp: 190–191 °C. IR (C_6H_6): ν(NH) 3340, ν(PtH) 1995, ν(CO) 1585 cm^{-1}. ^{31}P NMR (C_6D_6, 28 °C, δ): 33.38 (t), $J(^{195}Pt-^{31}P)$ = 2738 Hz. Anal. Calcd for $PtC_{44}H_{79}NO_2P_2$: C, 57.42; H, 8.86; N, 1.56. Found: C, 57.15; H, 8.72; N, 1.53.

2d: Recrystallized from *n*-hexane. Yield 47%. Mp: 169–172 °C. IR (C_6H_6): ν(NH) 3358, ν(PtH) 1995, ν(CO) 1588 cm^{-1}. Anal. Calcd for $PtC_{42}H_{77}NO_2P_2$: C, 57.97; H, 8.77; N, 1.58. Found: C, 57.22; H, 8.65; N, 1.51.

^{1}H NMR data for 2a–d are reported on Table I.

X-ray Data Collection. White crystals of 2a suitable for X-ray analysis were obtained by recrystallization from a toluene/*n*-hexane solution. A crystal of approximate dimensions of 0.3 × 0.2 × 0.2 mm was sealed in a Lindeman capillary under an argon atmosphere. It was mounted on a Philips PW 1100 computer-controlled four-circle diffractometer equipped with a graphite monochromator. Standard centering and auto-indexing proce-

Table I. ^{1}H NMR Data (C_6H_6, 28 °C, δ)[a] of 2

compnd	OH	=C=C–H(O–)	NH	*o*-CH	*m*-CH	*p*-CH	*o*-H[b]	*m*-H[b]	α-CH_2	β-CH_2/ CH_3/ CH_6H_{11}	C_6H_{11}	CH_3	PtH
2a	14.29 (d), *J* = 10.20	6.95 (d), *J* = 9.95, J^{195}Pt–^{1}H = 16.5	8.94 (s)	7.99 (d)	7.23 (dd)	6.84 (d)					2.23–1.10 (complex pattern)		–7.11 (t), J^{31}P–^{1}H = 16.3, J^{195}Pt–^{1}H = 657.9
2b	13.86 (d), *J* = 11.0	6.37 (d), *J* = 11.0	9.20 (s)				7.92 (d)	7.60 (d)			2.26–1.90 (complex pattern)		–7.13 (t), J^{31}P–^{1}H = 20, J^{195}Pt–^{1}H = 657
2c	14.58 (d), *J* = 10.02	6.81 (d), *J* = 9.20, J^{195}Pt–^{1}H = 17.5	6.52 (s)								2.26–1.24 (complex pattern)	1.57 (s)	–7.14 (t), J^{31}P–^{1}H = 16.5, J^{195}Pt–^{1}H = 643.5
2d	14.47 (d), *J* = 11.1	6.86 (d), *J* = 11.0	6.63 (s)						3.43 (m)	2.70–1.13 (complex pattern)			–6.95 (t), J^{13}P–^{1}H = 17.1, J^{195}–^{1}H = 639

[a] Chemical shifts in ppm, coupling constants in Hz. [b] Hydrogen atoms in ortho and meta position with respect to NO_2 group.

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(4) For a review, see: Geoffroy, G. L.; Bassner, G. L. *Adv. Organomet. Chem.* **1988**, *28*, 1.

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Table II. Crystal Data and Details of Measurements for 2a

formula	$C_{45}H_{75}NO_2P_2Pt$
mol wt	918.6
space group	$P2_1/c$
cell const	
a, Å	20.883 (12)
b, Å	12.017 (6)
c, Å	18.490 (8)
β, deg	108.00 (6)
cell vol, Å^3	4413.0
Z	4
D(calcd), g cm^{-3}	1.38
radiation	graphite monochromatized Mo Kα (0.7107 Å)
cryst size, mm	0.3 × 0.2 × 0.2
μ, cm^{-1}	31.44
diffractometer	Philips PW 1100
2θ range, deg	0–45
scan mode	θ–2θ
no. of collected rflns	10 374
no. of rflns with $I \geq 3\sigma(I)$	4267
R	0.068
R_w	0.071

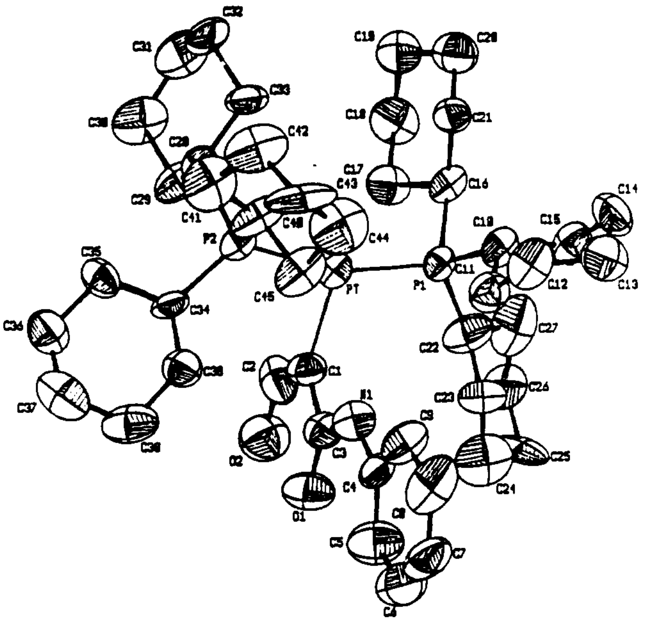

Figure 1. ORTEP diagram of **2a** with the labeling scheme for the non-hydrogen atoms.

dures[6] indicated the primitive monoclinic space group $P2_1/c$. The orientation matrix and accurate unit cell dimensions were determined from a least-squares fit of 25 symmetry-related reflections (10° ≤ 2θ ≤ 23°). Intensity data were collected at 24 °C using the $\theta - 2\theta$ scan method; two standard reflections, monitored every 150 reflection measurements, fluctuated within ±2% of their mean value. No absorption corrections have been applied. The intensities were corrected for Lorentz and polarization factors and scaled to give 4267 independent F_{hkl} values with $I \geq 3\sigma(I)$. Crystal data and details of data collection are listed in Table II.

Solution and Refinement of the Structure. The positions of Pt and P were determined from a three-dimensional Patterson synthesis. All the non-hydrogen atoms were located from subsequent Fourier maps and refined anisotropically. The positions of the H atoms were idealized, (except the enolic hydrogen atom) C–H 0.96 Å, assigned isotropic thermal parameters ($U_{(H)}$ = 1.2 Å U_{eq} (c)) and allowed to ride on their parent carbon atoms. The weighting scheme used in the final calculations was of the form $w^{-1} = a_j|F_o|^j$. The a_j parameters were calculated by using the program PESO.[7] Scattering factors for the atoms were taken from Cromer and Waber;[8] the scattering factors for Pt and P were corrected for the real and imaginary parts of the anomalous dispersion by using Cromer's values.[9] All computations were carried out on a CDC Cyber 76 computer using the programs of ref 10. The positional parameters of the non-hydrogen atoms are listed in Table III; the atom numbering scheme is shown in Figure 1.

Table III. Fractional Atomic Coordinates of the Non-Hydrogen Atoms for 2a

atom	x/a	y/b	z/c
Pt	0.7768 (0)	0.5186 (1)	0.6737 (0)
P(1)	0.8331 (2)	0.6439 (4)	0.7638 (2)
P(2)	0.7338 (2)	0.4277 (4)	0.5605 (2)
O(1)	0.6660 (7)	0.3520 (9)	0.8052 (8)
O(2)	0.7744 (7)	0.2490 (10)	0.3270 (8)
N(1)	0.6469 (8)	0.5030 (9)	0.7302 (9)
C(1)	0.7478 (9)	0.4040 (10)	0.7444 (9)
C(2)	0.7880 (10)	0.3180 (10)	0.7800 (10)
C(3)	0.6861 (9)	0.4150 (9)	0.7627 (9)
C(4)	0.5842 (6)	0.5410 (9)	0.7366 (8)
C(5)	0.5517 (6)	0.4940 (10)	0.7845 (8)
C(6)	0.4917 (6)	0.5390 (9)	0.7890 (8)
C(7)	0.4641 (6)	0.6330 (10)	0.7457 (8)
C(8)	0.4966 (6)	0.6800 (10)	0.6978 (8)
C(9)	0.5566 (6)	0.6350 (10)	0.6932 (8)
C(10)	0.7951 (9)	0.7860 (9)	0.7396 (9)
C(11)	0.7180 (10)	0.7850 (10)	0.7130 (10)
C(12)	0.6922 (9)	0.8990 (12)	0.6750 (10)
C(13)	0.7220 (10)	0.9960 (15)	0.7290 (9)
C(14)	0.7960 (9)	0.9910 (15)	0.7540 (10)
C(15)	0.8250 (10)	0.8810 (10)	0.7930 (10)
C(16)	0.0220 (9)	0.6620 (10)	0.7628 (9)
C(17)	0.9540 (10)	0.5440 (10)	0.7660 (9)
C(18)	0.0265 (9)	0.5580 (15)	0.7660 (9)
C(19)	1.0330 (10)	0.6230 (15)	0.6990 (9)
C(20)	1.0040 (9)	0.7360 (16)	0.6990 (9)
C(21)	0.9286 (9)	0.7290 (9)	0.6950 (9)
C(22)	0.8440 (9)	0.6130 (12)	0.8650 (9)
C(23)	0.7810 (9)	0.6240 (15)	0.8850 (9)
C(24)	0.7828 (10)	0.5648 (12)	0.9568 (9)
C(25)	0.8400 (10)	0.5866 (10)	1.0197 (9)
C(26)	0.9070 (9)	0.5710 (15)	1.0000 (10)
C(27)	0.9031 (10)	0.6480 (15)	0.9303 (10)
C(28)	0.8017 (8)	0.3870 (9)	0.5202 (9)
C(29)	0.8460 (10)	0.2960 (12)	0.5700 (9)
C(30)	0.901 (9)	0.2560 (15)	0.5380 (15)
C(31)	0.944 (9)	0.3530 (12)	0.5260 (9)
C(32)	0.902 (9)	0.4460 (15)	0.4770 (15)
C(33)	0.848 (9)	0.4860 (10)	0.5140 (9)
C(34)	0.6892 (8)	0.2970 (12)	0.5573 (9)
C(35)	0.6791 (9)	0.2220 (15)	0.4870 (9)
C(36)	0.6480 (9)	0.1090 (12)	0.4980 (9)
C(37)	0.5810 (9)	0.1200 (15)	0.5150 (12)
C(38)	0.5890 (9)	0.1970 (15)	0.5820 (9)
C(39)	0.6200 (9)	0.3080 (16)	0.5710 (9)
C(40)	0.6790 (9)	0.5260 (13)	0.4910 (9)
C(41)	0.6546 (10)	0.4993 (15)	0.4108 (10)
C(42)	0.6365 (12)	0.6192 (18)	0.3769 (10)
C(43)	0.5840 (10)	0.6820 (15)	0.4030 (15)
C(44)	0.6140 (10)	0.6917 (16)	0.4770 (14)
C(45)	0.6290 (9)	0.5780 (14)	0.5230 (9)

Scheme III

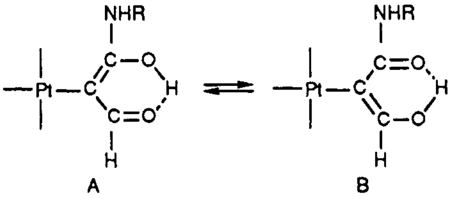

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Table IV. Selected Bond Distances (Å) and Bond Angles (deg) with the Estimated Standard Deviations for 2a[a]

Bond Distances			
Pt-P(1)	2.283 (5)	Pt-C(1)	2.11 (2)
Pt-P(2)	2.285 (5)	C(1)-C(2)	1.37 (3)
P(1)-C(10)	1.88 (2)	C(2)-O(2)	1.29 (2)
P(1)-C(16)	1.87 (2)	C(1)-C(3)	1.44 (3)
P(1)-C(22)	1.85 (2)	C(3)-O(1)	1.25 (2)
P(2)-C(28)	1.86 (2)	C(3)-N	1.36 (2)
P(2)-C(34)	1.82 (2)	N-C(4)	1.43 (2)
P(2)-C(40)	1.86 (2)	O(1)···O(2)	2.50 (2)
Bond Angles			
P(1)-Pt-P(2)	162.1 (2)	Pt-C(1)-C(3)	122.0 (9)
Pt-P(1)-C(10)	110.0 (6)	Pt-C(1)-C(2)	123.0 (9)
Pt-P(1)-C(16)	110.9 (6)	C(1)-C(2)-O(2)	126 (2)
Pt-P(1)-C(22)	118.9 (8)	C(1)-C(3)-O(1)	126 (1)
Pt-P(2)-C(28)	111.1 (6)	C(1)-C(3)-N	115 (1)
Pt-P(2)-C(34)	119.7 (6)	O(1)-C(3)-N	118 (1)
Pt-P(2)-C(40)	108.2 (8)	C(8)-N-C(4)	131 (1)
C(1)-Pt-P(2)	98.5 (5)	C(3)-C(1)-C(2)	115 (1)
C(1)-Pt-P(1)	99.3 (5)		

[a] Weighted least-squares plane and atomic deviations therefrom: $0.2795x + 0.6041y + 0.7463z - 15.85865 = 0$. Atoms in the plane and their deviations (Å): O(2)- (−0.004), O(1) (0.133), N (0.012), C(1) (−0.019), C(2) (−0.041), C(3) (0.052), C(4) (0.027), C(5) (0.010), C(6) (−0.023), C(7) (−0.039), C(8) (−0.023), C(9) (0.010).

Results and Discussion

The relevant metrical parameters of **2a** are given in Table IV with reference to Figure 1. The ligand lies almost exactly in a plane.

Planarity is accomplished thanks to systems involving on one hand resonance between the amide and its phenyl group and on the other hand a tautomerism between the enolic and the aldehydic group in the relative γ position (Scheme III). The former induces a planar conformation quite usual for amidic groups in open molecules,[11] the latter can be explaned in terms of the equilibrium.

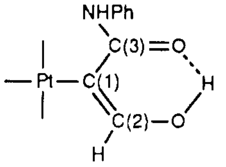
The conformational stability arising for this system accounts also for the short O(1)...O(2) nonbonded distance of about 2.50 Å. Also note that the bond angles ∠C-C-O(1) and ∠C-C-O(2) are widened to ~126° to relieve the corresponding interaction. The enolic hydrogen turns out to be either equally shared by O(1) and O(2) or to form a hydrogen bridge between them. Hereby the possibility of an unsaturated vinyl alcohol which is known to be relatively unstable exists.

The presence of a tautomeric system is confirmed by the metrical parameters of the ligand. Table IV shows that all the single bonds are shorter and the double bonds are longer than the normal values[12] for either A or B, giving reason of the suggested equilibrium, even though the limiting form, B, seems to be predominant.

The plane defined by the ligand bisects the bond angle ∠P(1)-Pt-P(2) and is normal to the coordination plane of Pt. This conformation has been previously observed in several σ-aryl and σ-vinyl platinum compounds all having a trigonal carbon atom bonded to the metal.[13] It derives from requirements of best overlapping between π- and π^*-orbitals of the ligand and hybrid sp^2d orbitals of Pt. Probably this fact gives also reason of the low reactivity of the carbon atom bonded to Pt.

In the Experimental Section and in Table I are reported ^1H and ^{31}P NMR data for **2a–d**. The most relevant points are: (i) the equivalence of the two phosphorous atoms bonded to the platinum, (ii) the absence of signals due to aldehydic protons, (iii) the presence of doublets (6.86–6.37 ppm) showing the coupling with the platinum assigned to the vinyl protons bonded to the carbon atom, (iv) the presence of enolic proton doublets at 14.58–13.86 ppm, coupled with the vinyl proton.

IR data confirm these findings. The spectra show signals at 3340–3260 cm^{-1} and at 1606–1585 cm^{-1} attributable to NH and CO amidic stretchings; also evident are the absence of signals due to aldehydic groups. These results together with the structural parameters and in particular the bond lengths C(1)–C(3) = 1.44, C(1)–C(2) = 1.36, C(2)–O(2) = 1.29, and C(3)–O(1) = 1.25 Å lead to the more favored structural picture of **2a** in terms of formula 2, in which vinyl–enolic group is present.



2a

We are currently investigating the reactions of carbon suboxide with organometallic compounds in order to explain the factors causing mono- or diinsertion reactions[14] with respect to the metal, and the addition reaction of bases to ketenyl metal complexes.

Acknowledgment. This work was supported by Ministero della Pubblica Istruzione (Roma) and by the Consiglio Nazionale delle Ricerche (CNR, Roma). We are very indebted to Dr. S. Mammi for execution of ^1H NMR spectra of **2a,c** and to Mr. G. Ravazzolo for technical assistance.

Supplementary Material Available: Tables of thermal parameters of the non-hydrogen atoms and positional parameters of the hydrogen atoms for **2a** (5 pages); a listing of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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