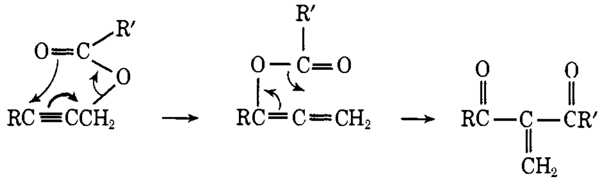
Table II. Yields of α,β-Unsaturated Ketones from the Pyrolysis of Propargyl Esters

Propargyl ester	Pyrolysis temp, °C	Product	Yield, %[a]	Recovered starting material, %[a]
$\mathrm{PhC{\equiv}CCH_2OCOH}$[b]	670	$\mathrm{PhCOCH{=}CH_2}$	94	Trace
	640		82	16
	560		34	55
$\mathrm{HC{\equiv}CCH_2OCOPh}$[c]	660	$\mathrm{PhCOCH{=}CH_2}$	80	3
	640		82	8
$\mathrm{HC{\equiv}CCH(Ph)OCOCH_3}$[d]	645	$\mathrm{CH_3COCH{=}CHPh}$	79	7
	640		87	7
	670		48	4
$\mathrm{HC{\equiv}CCH_2OCOPh}$[e]	630	$\mathrm{PhCOCH{=}CH_2}$	54	11
	630		56	10
$\mathrm{HC{\equiv}CCH_2OCOCH_3}$[c]	630	$\mathrm{CH_3COCH{=}CH_2}$	60	Trace

[a] Yields determined by nmr spectroscopy using an internal standard, ethyl benzoate or propiophenone. [b] This ester was prepared from the alcohol and 97% formic acid. See ref 5. [c] See ref 4 and A. M. Sladkov, V. V. Korshak, and A. G. Makhsumov, *Vysokomol. Soedin.*, **6**, 1642 (1964); *Chem. Abstr.*, **61**, 14163 (1964). [d] See ref 4 and M. Barrelle, D. Plovin, and R. Glenat, *Bull. Soc. Chim. Fr.*, 449 (1967). [e] See ref 4 and 5.

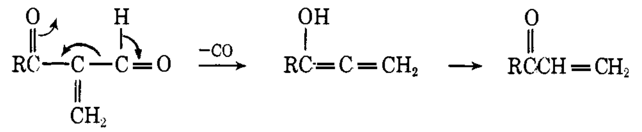
of propargyl esters to allenyl esters have been reported,[10]



and vinyl esters are known to undergo 1,3-acyl shifts in the gas phase at 500–600°.[11]

Instead of alkylidenediones, α,β-unsaturated ketones are obtained from the pyrolysis of propargyl esters which would give rise to alkylidenediones that have a hydrogen atom attached to one carbonyl group. In Table II are listed the yields of the α,β-unsaturated ketones obtained from various propargyl esters. The products were identified by their nmr spectra which, with the exception of the new compound cyclohexyl vinyl ketone,[12] were compared with spectra of commercial samples or published data.

An attractive explanation for these results is that the intermediate enedione undergoes a facile decarbonylation reaction to give an enol which rearranges to the ketone.



Since propargyl alcohol is readily available and inexpensive, the pyrolysis of propargyl esters offers a synthetically useful means of preparing vinyl ketones in reasonable yields from the corresponding carboxylic acid.

$$\mathrm{RCOOH} + \mathrm{HOCH_2C{\equiv}CH} \xrightarrow[\text{2. pyrolysis}]{\text{1. esterification}} \mathrm{RCOCH{=}CH_2} + \mathrm{CO}$$

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(10) (a) A. I. Zakharova, *Zh. Obshch. Khim.*, **15**, 429 (1949); (b) P. D. Landor and S. R. Landor, *J. Chem. Soc.*, 1015 (1956); (c) G. Saucy, R. Marbert, H. Lindlarand, and O. Isler, *Helv. Chim. Acta*, **42**, 1945 (1959); (d) V. T. Ramakrishnan, K. V. Narayanan, and S. Swaminathan, *Chem. Ind.* (*London*), 2082 (1967); (e) W. R. Benn, *J. Org. Chem.*, **33**, 3113 (1968).

(11) (a) A. B. Boese, Jr., and F. G. Young, Jr., U. S. Patent 2,395,800 (1946); *Chem. Abstr.*, **40**, 3130 (1946); (b) F. G. Young, F. C. Frostick, Jr., J. J. Sanderson, and C. R. Hauser, *J. Amer. Chem. Soc.*, **72**, 3635 (1950).

(12) This compound gave an acceptable elemental analysis by Spang Microanalytical Laboratory, Ann Arbor, Mich.

(13) Alfred P. Sloan Research Fellow, 1970–1972.

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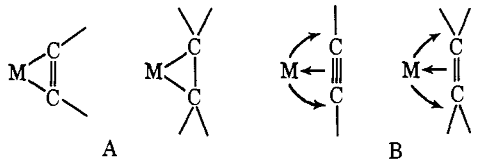
A Comparison of the Bonding in Zero- and Divalent Platinum–Olefin and –Acetylene Complexes from Carbon-13 Nuclear Magnetic Resonance Parameters[1]

Sir:

Metal–olefin and –acetylene bonding is dominated by the relative energies of the π and π^* orbitals of the unsaturated hydrocarbon and the metal dsp hybrid orbitals used in the bonding.[2] This model leads to a continuum of bonding and incorporates the original Chatt–Dewar–Duncanson[3] bonding descriptions shown below.



Much debate has been devoted (a) to an appraisal of the relative magnitudes of the σ and π interactions, (b) to the choice of metal orbitals employed in the bonding, and hence (c) to the formal oxidation state and coordination number of the metal.[4–8] We wish to present the

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(1) Part XXII. For part XXI, see A. H. Lawrence, D. R. Arnold, J. B. Stothers, and P. Lapouyade, *Tetrahedron Lett.*, in press.

(2) E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Can. J. Chem.*, **46**, 3879 (1968).

(3) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, 79 (1951); J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

(4) M. A. Bennett, Second Coordination Conference of the Coordination and Metal Organic Chemistry Division of the Royal Australian Chemical Institute, Monash, Australia, May 1968.

(5) F. R. Hartley, *Chem. Rev.*, **69**, 799 (1969), and references cited therein.

(6) (a) J. H. Nelson, K. S. Wheelock, L. C. Cusachs, and H. B. Jonassen, *J. Amer. Chem. Soc.*, **91**, 7005 (1969); (b) *ibid.*, **92**, 5100 (1970).

(7) J. H. Nelson and H. B. Jonassen, *Coord. Chem. Rev.*, **6**, 27 (1971).

(8) V. Belluco, B. Crociani, R. Pietropaolo, and P. Uguaglia, *Inorg. Chim. Acta*, 19 (1969).

Table I. ^{13}C Nmr Parameters[a] for Some Olefin and Acetylene Complexes of Platinum

	Olefinic or acetylenic carbons			Platinum–methyl			Other		
Compound, Q = PMe$_2$Ph	δ_C	$J(^{195}Pt-^{13}C)$	Other	δ_C	$J(^{195}Pt-^{13}C)$	$J(^{31}P-^{13}C)$	δ_C	$J(^{195}Pt-^{13}C)$	$J(^{31}P-^{13}C)$
trans-[PtMe(C$_2$H$_4$)Q$_2$]$^+$PF$_6$$^-$	84.4	50 ± 3		5.6	615 ± 6	6 ± 2	10.5[d]	16 ± 2	18 ± 2
trans-[PtMe(MeC≡CMe)Q$_2$]$^+$PF$_6$$^-$	69.5	18 ± 3		−4.2	632 ± 4	6 ± 2	11.4[d]	18 ± 2	18 ± 2
K$^+$[PtCl$_3$(C$_2$H$_4$)]$^-$	67.1	195 ± 2							
(COD)PtMe$_2$[b]	98.8	55 ± 3		4.7	773 ± 3		29.9	<3	
(COD)Pt(CF$_3$)$_2$	111.0	56 ± 3					29.4	<3	
(COD)PtI$_2$	103.2	124 ± 4					31.8	<3	
(PPh$_3$)$_2$Pt(C$_2$H$_4$)	39.6	194 ± 2	24[c] ± 2						
(PPh$_3$)$_2$Pt(MeC≡CMe)	112.8	52 ± 3	27[c] ± 3				10.4[e]	9 ± 2	

[a] Obtained at 25.2 MHz with a Varian XL-100-15 system operating in the Fourier transform mode. CD$_2$Cl$_2$ solutions (25–30% w/v) were examined (*ca.* 36°). Shieldings (δ_C) given relative to TMS (±0.1 ppm), increasing positive values toward lower fields; *J* values in hertz. [b] COD = 1,5-cyclooctadiene. For the free ligand the shieldings are δ_C 28.2 (CH$_2$) and 128.5 (=CH). [c] $^3J + {}^1J(^{31}P-^{13}C)$. [d] Phosphine-methyl carbons. [e] Methyl carbons.

^{13}C nmr parameters for a series of simple olefin and acetylene complexes of Pt(0) and Pt(II) to illustrate the potential of ^{13}C nmr spectroscopy in the elucidation of the metal–carbon bonding in these species.

Olefinic carbons show a marked increase in shielding on coordination to platinum absorbing 17–83 ppm upfield from the free olefin (see Table I) in the order {P(C$_6$H$_5$)$_3$}$_2$Pt(C$_2$H$_4$) > [PtCl$_3$(C$_2$H$_4$)]$^-$ > *trans*-[PtCH$_3$(C$_2$H$_4$){P(CH$_3$)$_2$C$_6$H$_5$}$_2$]$^+$ and CODPt(CH$_3$)$_2$ > CODPt(CF$_3$)$_2$, where COD = 1,5-cyclooctadiene. This suggests that the increased shielding correlates with metal d to olefin-π^* bonding.[9] Previous ^{13}C nmr studies of olefins coordinated to Ag$^+$ [10] and Rh(I)[11] showed increased shieldings of the complexed olefinic carbons ranging from +4 to +115 ppm, respectively, which is consistent with this view. However, the shielding order for the acetylenic carbons is *trans*-[PtCH$_3$(CH$_3$C≡CCH$_3$){P(CH$_3$)$_2$C$_6$H$_5$}$_2$]$^+$ > CH$_3$C≡CCH$_3$ > {P(C$_6$H$_5$)$_3$}$_2$Pt(CH$_3$C≡CCH$_3$). The complexity of factors influencing the ^{13}C shieldings of coordinated olefinic and acetylenic carbons is evident even from the CDD pictorial descriptions A and B.

In hydrocarbons the ^{13}C shieldings are primarily governed by the hybridization and electron density of the individual nuclei.[12] Consequently the "metallocyclic" structure A, which implies a rehybridization of the olefin/acetylene carbons, *viz.* acetylene sp to sp^2 and olefin sp^2 to sp^3, offers a straightforward explanation of the ^{13}C shieldings of the zerovalent platinum complexes. However, an interpretation may be based on B by considering the following. Metal to ligand-π^* interaction (i) increases the total electron density at the olefinic/acetylenic carbons and (ii) reduces the carbon–carbon π-bond order and hence the π character of these carbons. Ligand-π to metal dsp bonding (iii) decreases the π character and (iv) decreases the electron density at the olefinic/acetylenic carbons. For coordinated olefinic carbons an increased ^{13}C shielding arising from factors i, ii, and iii is only opposed by factor iv. Therefore, it is reasonable to expect that stable metal–olefin complexes will show a net increase in shielding for these carbons, the magnitude of which will correlate closely with the electron density on the metal and metal to olefin π^* bonding.[13] For coordinated acetylenes a decrease in acetylenic π character is equivalent to an increase in olefin π character; thus factors ii, iii, and iv favor a deshielding and are only opposed by factor i. Consequently we expect that the shieldings of acetylenic carbons in stable metal–acetylene complexes will fall in the range δ_C(sp) to δ_C(sp^2) and that the deshielding will roughly correlate with metal to acetylene π^* bonding.[14]

^{13}C–X spin–spin coupling interactions tend to be dominated by the Fermi contact term such that the hybridization of the interacting nuclei is reflected, at least crudely, by the $J(^{13}C-X)$ values.[12a,15] The origins of $^1J(^{195}Pt-^{13}C)$ in platinum–olefin and -acetylene complexes are not yet fully established. The observation that $^1J(^{195}Pt-^{13}C)$ for the olefinic carbons in *trans*-[PtCH$_3$(C$_2$H$_4$){P(CH$_3$)$_2$C$_6$H$_5$}$_2$]$^+$ is greater than $^1J(^{195}Pt-^{13}C)$ for the acetylenic carbons in *trans*-[PtCH$_3$(C$_3$C≡C-CH$_3$){P(CH$_3$)$_2$C$_6$H$_5$}$_2$]$^+$ indicates that the mode of transmission for this coupling is more efficient for olefins than acetylenes, but the fact that the same trend is observed for the zerovalent complexes indicates the naivety[6b] of the "metallocyclic" description A. For the latter we would expect[15] $^1J(^{195}Pt-^{13}C_{sp^2})$ for the acetylene complex to be greater than $^1J(^{195}Pt-^{13}C_{sp^3})$ for the ethylene complex. The similarity of the ratio of $^1J(^{195}Pt-^{13}C)$ for the olefinic to acetylenic carbons in both {P(C$_6$H$_5$)$_3$}$_2$Pt(un) and *trans*-[PtCH$_3$(un){P(CH$_3$)$_2$C$_6$H$_5$}$_2$]$^+$, where un = C$_2$H$_4$ and CH$_3$C≡CCH$_3$, suggests that the mechanism of this coupling is independent of the formal oxidation state of the metal, the latter merely contributing to the magnitude of this coupling: $^1J(^{195}Pt-^{13}C)$Pt(0) > Pt(II). This is turn suggests that the bonding in zero- and divalent platinum complexes differs only in magnitude and not in mode.

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(9) $\Delta\delta_C$, the increased shielding, correlates with $\Delta\nu_{str}$(C=C) in these compounds.

(10) R. G. Parker and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 743 (1970).

(11) G. M. Bodner, B. N. Storhoff, D. Doddrell, and L. J. Todd, *Chem. Commun.*, 1530 (1970).

(12) (a) J. B. Stothers in "Carbon-13 Nmr Spectroscopy," Academic Press, New York, N. Y., 1971. (b) For example, ethane and ethylene have shieldings of 5.9 and 122.8 ppm (from TMS), respectively, while the C-2 shieldings of butane, 2-butyne, and *cis*-2-butene are 25.0, 73.9, and 124.3 ppm, respectively.

(13) Deshielding associated with iv is only likely to be important if olefin-π to metal dsp bonding exceeds metal to olefin-π^* interaction. The olefinic carbons of cyclopentene and cyclohexene complexes with Ag$^+$, for which olefin-π to metal σ bonding > metal to olefin-π^* interaction, show increased shielding ~4 ppm; see ref 10.

(14) Since ^{13}C shieldings are dominated by the paramagnetic term [M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963)], other contributing factors within this term may limit the generality of these predictions.

(15) We have recently shown that $^1J(^{195}Pt-^{13}C)$ values for several Pt–C σ bonds support this view: M. H. Chisholm, H. C. Clark, L. E. Manzer, and J. B. Stothers, *Chem. Commun.*, 1627 (1971).

The ^{13}C parameters for $CODPtX_2$, where X = CH_3, CF_3, and I and COD = 1,5-cyclooctadiene,[16] demonstrate that $^1J(^{195}Pt-^{13}C)$ for the olefinic carbons is dependent on the trans ligand and hence the Pt 6s orbital contribution to the Pt hybrid orbital used in the olefin-π to platinum σ bond (see B). In support of Braterman's[17] explanation for $^2J(^{195}Pt-^1H)$ we find $^1J(^{195}Pt-^{13}C)$ increases as the trans influence of X decreases: $CH_3 \sim CF_3 > I$.[18,19] $^1J(^{195}Pt-^{13}C)$ does not correlate with the increased shielding of the olefinic carbons and is therefore independent of platinum to olefin-π^* bonding. These findings parallel previous studies of $^1J(^{183}W-^{31}P)$ which were shown to be independent of W-P π bonding.[20]

We conclude that our ^{13}C parameters strongly support the concept of a continuum of bonding in platinum-olefin/acetylene complexes (based on B) and that $^1J(^{195}Pt-^{13}C)$ to the olefinic/acetylenic carbons is dominated by the Pt 6s orbital contribution to the olefin/acetylene-π to metal σ bond. A comparison of olefin and acetylene bonding in *trans*-$[PtCH_3(un)\{P(CH_3)_2C_6H_5\}_2]^+$, un = C_2H_4 and $CH_3C{\equiv}CCH_3$, suggests that ethylene is both a stronger σ donor[21] and a stronger π acceptor[22] than 2-butyne. Furthermore the ^{13}C parameters for $\{P(C_6H_5)_3\}_2Pt(un)$, un = C_2H_4 and $CH_3C{\equiv}CCH_3$, lend no obvious support to the suggestion[7] that metal-acetylene bonding is stronger than metal-olefin bonding when both acetylenic π orbitals can participate.

[16] H. C. Clark and L. E. Manzer, *J. Organometal. Chem.*, **38**, C41 (1972).

[17] P. S. Braterman, *Inorg. Chem.*, **5**, 1085 (1966).

[18] T. G. Appleton, M. H. Chisholm, H. C. Clark, and L. E. Manzer, *ibid.*, in press.

[19] The same order of $^2J(^{195}Pt-^1H)$ for the olefinic protons is observed.

[20] G. G. Mather and A. Pidcock, *J. Chem. Soc. A*, 1226 (1970).

[21] From a comparison of $^1J(^{195}Pt-^{13}C)$ for the platinum methyl group; see discussion in ref 15.

[22] From a comparison of (i) the relative shieldings of the platinum methyl carbons (see Table I), and (ii) $^3J(^{195}Pt-^1H)$ and $^2J(^{195}Pt-^{13}C)$ for the phosphine methyls: see discussion, M. H. Chisholm and H. C. Clark, *Inorg. Chem.*, **10**, 2557 (1971).

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Dansylglycine as a Fluorescent Probe for Aqueous Solutions of Cationic Detergents

Sir:

Aminonaphthalenesulfonate (ANS) compounds have recently been employed as fluorescent probes to study protein conformational changes and binding properties.[1-12] Upon binding to a low dielectric constant region of the protein, blue shifts and increased emission intensity are observed. ANS derivatives have also been used to study incorporation into biological membranes.[13] In this report we describe experiments where we have employed dansylglycine (1-dimethylaminonaphthalene-5-sulfonylglycine) to study the behavior of cationic detergents in water solution.

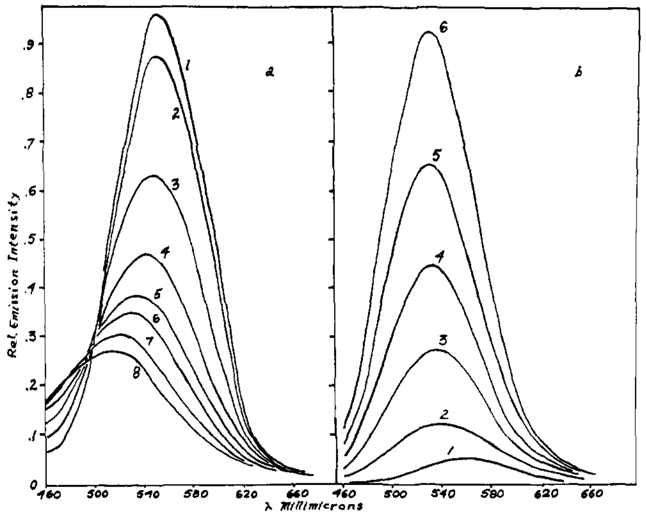

Figure 1. (a) Fluorescence emission of 6.5 × 10^{-5} *M* dansylglycine in the presence of CPBr, irradiated at 370 nm. Numbers refer to CPBr concentration: 1, 0 *M;* 2, 8.66 × 10^{-5} *M;* 3, 17.4 × 10^{-5} *M;* 4, 25 × 10^{-5} *M;* 5, 33 × 10^{-5} *M;* 6, 42 × 10^{-5} *M;* 7, 58.7 × 10^{-5} *M;* 8, 84.8 × 10^{-5} *M*. (b) Emission of 6.5 × 10^{-5} *M* DG in the presence of Cetab. Detergent concentration: 1, 0 *M;* 2, 1.68 × 10^{-4} *M;* 3, 2.52 × 10^{-4} *M;* 4, 3.36 × 10^{-4} *M;* 5, 5.04 × 10^{-4} *M;* 6, 8.4 × 10^{-4} *M*. Relative intensity data are arbitrary and are not interchangeable for the two sets of data. Emission of DG in the presence of CPCl behaves almost identically with that seen in Figure 1a. Emission spectra are not corrected for photomultiplier sensitivity.

Samples of the detergents cetyltrimethylammonium bromide (Cetab), cetylpyridinium bromide (CPBr), and cetylpyridinium chloride (CPCl) were crystallized several times from acetone-water. Dansylglycine (DG), mp 157-157.5°, lit.[14] 158°, was used without further purification.

In one set of experiments we have irradiated aqueous solutions of 6.5 × 10^{-5} *M* DG in the cavity of an Aminco-Bowman spectrofluorimeter in the presence of a range of concentrations of Cetab, CPBr, or CPCl. Emission changes of DG in the presence of Cetab and CPBr are shown in Figure 1. When CPCl was used, results were almost identical with those shown in Figure 1a. Figure 2 shows the intensity of DG fluorescence as a function of detergent concentration for several DG concentrations. Extrapolations of the changing and unchanging regions of the plots give values of roughly 9 × 10^{-4} *M* and 4-5 × 10^{-4} *M* at the break points for Cetab and CPCl, respectively. For CPBr (not shown) a value of about 3 × 10^{-4} *M* was found at the break point. No particular dependence of the apparent break point on DG concentration was noted. The previously reported critical micelle concentrations (cmc's) for these surfactants are about 9 × 10^{-4}, 6-9 × 10^{-4}, and 6-7.5 × 10^{-4} *M* for Cetab, CPCl, and CPBr,

[1] R. F. Chen, *Arch. Biochem. Biophys.*, 120, 609 (1967).

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[3] H. Takashina, *Biochem. Biophys. Acta*, **200**, 319 (1970).

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[12] H. M. Winkler, *ibid.*, **8**, 2586 (1969).

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